On Multiplication of Determinants in Banach Spaces

by

R. SIKORSKI

Communicated by K. KURATOWSKI at the meeting of March 16, 1953

Let X be a Banach space, let Ξ be a closed subspace of the Banach space X^* of all linear (= continuous and additive) functionals on X; and let $\Re$ be a closed subspace of the Banach space of all linear transformations of Ξ into Ξ, such that: 1^0 $\Re$ contains the identical mapping I of Ξ into Ξ; 2^0 if $K_1, K_2 \in \Re$, then the superposition $K_1 K_2 \in \Re$; 3^0 if $K \in \Re$, $x \in X$ and $\varphi \in \Xi$, then $K_{\varphi,x} \in \Re$ where $K_{\varphi,x}$ denotes the linear operation defined on Ξ by the equation

$$K_{\varphi,x}(\psi) = K(\psi)(x) \cdot \varphi \qquad \text{for} \qquad \psi \in \Xi.$$

Each functional F on $\Re$ determines a linear transformation T_F of Ξ into X^* defined as follows:

$$T_F(\varphi)(x) = F(I_{\varphi,x}) \qquad \text{for} \qquad \varphi \in \Xi, \, x \in X,$$

where $I_{\varphi,x}(\psi) = \psi(x) \cdot \varphi$ for $\psi \in \Xi$.

Let $\mathfrak{M}$ be the Banach space of all linear functionals F on $\Re$, such that $T_F \in \Re$ and

$$T_{F_K} = K T_F \qquad \text{for each} \qquad K \in \Re,$$

where F_K denotes the linear functional on $\Re$ defined by the equation

$$F_K(M) = F(MK) \qquad \text{for} \qquad M \in \Re.$$

Leżański [2] has proved that $\mathfrak{M}$ is a Banach algebra with the following definition of the product $F \cdot G$ of two functionals $F, G \in \mathfrak{M}$:

$$F \cdot G(K) = G(K T_F) \qquad \text{for} \qquad K \in \Re.$$

Notice that

(1) $$T_{F \cdot G} = T_F T_G, \qquad T_{F+G} = T_F + T_G.$$

Leżański [1] has proved that the functional

$$(2) \qquad D(F) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \begin{vmatrix} F(I), & n-1, & 0, & 0 ,\ldots, & 0, & 0 \\ F^2(I), & F(I), & n-2, & 0 ,\ldots, & 0, & 0 \\ F^3(I), & F^2(I), & F(I), & n-3,\ldots, & 0, & 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ F^{n-1}(I), & F^{n-2}(I), & \cdots\cdots\cdots\cdots, & F(I), & 1 \\ F^n(I), & F^{n-1}(I), & \cdots\cdots\cdots\cdots, & F^2(I), & F(I) \end{vmatrix}$$

has the following property: the linear equation

$$(3) \qquad\qquad (I + T_F)(\varphi) = \psi \qquad\qquad (\varphi, \psi \, \epsilon \, \varXi)$$

has a (necessarily unique) solution φ for every $\psi \, \epsilon \, \varXi$ if and only if $D(F) \neq 0$.

Leżański's original definition of the functional $D(F)$, which should be called the determinant of equation (3), is not the same as the above definition which is similar to Ruston's [4, 5] definition. Notice that, in general, $D(F)$ is not determined by (3) (i. e. by the linear operation T_F) since the transformation $F \to T_F$ need not be one-to-one.

Theorem. *If* $F, G \, \epsilon \, \mathfrak{M}$, *and if*

$$(4) \qquad\qquad F_1 \cdot F_2 \cdot \ldots \cdot F_n(I) = F_2 \cdot \ldots \cdot F_n \cdot F_1(I)$$

for each finite sequence $\{F_i\}$ *such that* $F_i =$ *either* F *or* G, *then*

$$(5) \qquad\qquad D(F + G + F \cdot G) = D(F) \cdot D(G).$$

In other words:

The determinant of the linear equation

$$(I + T_F)(I + T_G)(\varphi) = \psi,$$

i. e. of the equation (see (1))

$$(I + T_{F+G+F \cdot G})(\varphi) = \psi,$$

is the product of the determinants of the linear equations

$$(I + T_F)(\varphi) = \psi, \qquad (I + T_G)(\varphi) = \psi.$$

This theorem is a generalization of a result of Leżański [2] who has proved that equation (5) holds under the more restrictive hypothesis that $F \cdot G = G \cdot F$.

The proof [*]) is based on the statement (Leżański [2]; see also Plemelj [3], p. 122) that for $||F|| < 1$

$$D(F) = \exp\left(\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} F^n(I) \right) = \exp\left(\varPhi\left(\log(E + F) \right) \right)$$

where E is the unit element added to the algebra $\mathfrak{M}$, and $\varPhi(F) = F(I)$ for $F \, \epsilon \, \mathfrak{M}$. The following lemma plays an essential part:

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[*]) The complete proof will appear in Studia Mathematica **14** (1953).

Lemma. *Let* $a_1, \ldots, a_m$ *be a sequence formed of letters* a *and* b *exclusively, such that each of the letters* a, b *appears at least once. The sum of the numeral coefficients at all products of the form*

$$a_k \ldots a_m\, a_1 \ldots a_{k-1} \qquad\qquad (k = 1, \ldots, m)$$

in the formal expansion of

$$\log\left((1 + a)(1 + b)\right) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n}\, (a + b + ab)^n$$

(where $ab \neq ba$*) is equal to* 0.

Notice that the condition (4) holds if X and $\varXi$ are the spaces L, M, L^p, C or: l, m, l^p, c, and equation (3) is of the integral type

$$\varphi(s) + \int T(s, t)\, \varphi(t)\, dt = \psi(s)$$

or: it is a system of linear equations

$$\varphi_i + \sum_{k=1}^{\infty} T_{ik}\, \varphi_k = \psi_i, \quad i = 1, 2 \ldots.$$

Institute of Mathematics, Polish Academy of Sciences

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Sur la structure de l'ensemble engendré par les intégrales tendant vers le point singulier du système d'équations différentielles

par

Z. SZMYDT

Présenté par T. WAŻEWSKI à la séance du 22 Juin 1953

Définition. Une matrice réelle sera dite être du type L lorsque les parties réelles de toutes ses racines caractéristiques sont différentes de zéro. Par le plan caractéristique négatif (positif) de la matrice A du type L nous allons entendre l'hyperplan maximal invariant par rapport à la transformation linéaire, définie par la matrice A, l'hyperplan qui ne contient aucune direction caractéristique correspondante à une racine caractéristique ayant la partie réelle positive (négative).

Théorème 1. *Considérons le système d'équations différentielles*

(1) $$dy_i/dt = F^{(i)}(y_1, \ldots, y_n) \qquad (i = 1, \ldots, n)$$

et supposons que les fonctions $F^{(i)}$ soient continues dans le voisinage du point $\Theta = (0, \ldots, 0)$, $F^{(i)}(\Theta) = 0$, et que $F_{y_j}^{(i)}(\Theta)$ existent et soient finis. Posons

$$a_{ij} = F_{y_j}^{(i)}(\Theta), \quad \varphi^{(i)}(y_1, \ldots, y_n) = F^{(i)}(y_1, \ldots, y_n) - \sum_{j=1}^{n} a_{ij} y_j.$$

Supposons que la matrice $\|a_{ik}\|$ soit une matrice du type L, dont le plan caractéristique négatif N est un plan à q dimensions, $0 < q < n$ et que tous les quatre nombres dérivés (supérieur, inférieur, à droite et à gauche) de la fonction $\varphi^{(i)}(y_1, \ldots, y_n)$ ($i = 1, \ldots, n$) relatifs à chacune des variables y_i séparément soient bornés dans le voisinage du point Θ et continus au point Θ.

Dans ces hypothèses il existe un voisinage fermé du point Θ (image homéomorphe d'une sphère fermée à n dimensions) jouissant de cette propriété que la totalité des trajectoires du système (1) contenues dans ce voisinage et tendant vers Θ lorsque $t \to +\infty$ engendre un ensemble Q constituant l'image homéomorphe d'une sphère fermée à q dimensions. Q est un ensemble unifolié par rapport au plan N, c. à. d. qu'il ne possède plus qu'un seul point

commun avec tout plan parallèle au plan positif. La surface Q possède presque partout le plan tangent, qui au point Θ coïncide avec le plan N.

Pour éviter la complication des calculs je me bornerai à la démonstration du Théorème 1 au cas particulier où toutes les racines caractéristiques $\lambda_i (i = 1, \ldots, n)$ de la matrice $\|a_{ij}\|$ sont réelles. La démonstration du cas général est tout à fait analogue.

Posons

$$(2) \qquad \lambda = \min (|\lambda_1|, \ldots, |\lambda_{n-1}|, |\lambda_n|), \qquad \varrho = \frac{\lambda}{3n},$$

Par l'intérmediaire d'une transformation affine aux coefficients constants, convenablement choisie, on obtient du système (1) le système

$$(3) \qquad dx_i/dt = \lambda_i x_i + \varrho_i x_{i+1} + \varepsilon_i(X) \quad (i = 1, \ldots, n)$$

où

$$X = (x_1, \ldots, x_n), \quad \lambda_i < 0 \, (i = 1, \ldots, q), \quad \lambda_i > 0 \quad (i = q+1, \ldots, n),$$

$$(4) \qquad 0 \leqslant \varrho_i < \varrho \quad (i = 1, \ldots, n), \quad \varrho_q = \varrho_n = 0,$$

$$\eta_i(X) = |\varepsilon_i(X)| \, |X|^{-1} \to 0 \quad \text{lorsque} \quad |X| \to 0.$$

Voici maintenant un lemme qui nous sera utile dans la démonstration du Théorème 1 par une méthode topologique de T. Ważewski [1].

Lemme 1. Il existe un voisinage fermé $V(\Theta, \delta)$ du point Θ et du rayon δ tel, que la totalité des trajectoires du système (3), contenues dans $V(\Theta, \delta)$ et tendant vers Θ lorsque $t \to +\infty$, constitue un ensemble unifolié par rapport au plan $x_{q+1} = x_{q+2} = \ldots = x_n = 0$.

Si le nombre positif δ est suffisamment petit on a pour $i = 1, \ldots, n$

$$(5) \qquad |\varepsilon_i(X^{(1)}) - \varepsilon_i(X^{(2)})| < \varrho \sum_{j=1}^{n} |x_j^{(1)} - x_j^{(2)}| \quad \text{lorsque} \quad |X^{(1)}| \leqslant \delta, |X^{(2)}| \leqslant \delta.$$

Soient $X^{(1)}(t) = (x_1^{(1)}(t), \ldots, x_n^{(1)}(t))$, $X^{(2)}(t) = (x_1^{(2)}(t), \ldots, x_n^{(2)}(t))$ deux intégrales du système (3) qui à l'instant $t = t_0$ traversent le plan $x_i = \xi_i$ $(i = 1, \ldots, q)$ et sans quitter le voisinage $V(\Theta, \delta)$ tendent vers Θ lorsque $t \to +\infty$. On aura pour $s = 1, 2$

$$x_i^{(s)} = \xi_i e^{\lambda_i(t-t_0)} + e^{\lambda_i t} \int_{t_0}^{t} e^{-\lambda_i \tau} \{\varepsilon_i(X^{(s)}(\tau)) + \varrho_i x_{i+1}^{(s)}(\tau)\} \, d\tau \quad (i = 1, \ldots, q),$$

$$(6)$$

$$x_i^{(s)} = - e^{\lambda_i t} \int_{t}^{+\infty} e^{-\lambda_i \tau} \{\varepsilon_i(X^{(s)}(\tau)) + \varrho_i x_{i+1}^{(s)}(\tau)\} \, d\tau \quad (i = q+1, \ldots, n).$$

Désignons par

$$\alpha = \max_{(i)} \sup_{t_0 \leqslant t < +\infty} |x_i^{(1)} - x_i^{(2)}|.$$

En vertu de (6), (5), (4), (2) on obtient $|x_i^{(1)} - x_i^{(2)}| \leqslant \dfrac{2 \varrho n \alpha}{\lambda} = \tfrac{2}{3} \alpha$ pour $t \geqslant t_0$,

$(i = 1, \ldots, n)$, d'où il résulte, tenant compte de la définition du nombre α, que $\alpha \leqslant \frac{2}{3}\alpha$. On a donc $\alpha = 0$, ce qui signifie que $X^{(1)}(t) = X^{(2)}(t)$, lorsque $t \geqslant t_0$.

Pour la démonstration du Théorème 1 nous allons introduire quelques fonctions et quelques ensembles auxiliaires. Soit

$$r(t) = e^{Bt}, \quad \text{où} \quad -\lambda + \varrho < B < 0,$$

(ensemble $\overline{W}(\tau)$) $\quad \tau \leqslant t, \sum_{i=1}^{q} x_i^2 \leqslant r^2(t), \quad \sum_{i=q+1}^{n} x_i^2 \leqslant \sum_{i=1}^{q} x_i^2$

$$\mu(\tau) = \left| \; sup \; \sqrt{\sum_{i=1}^{n} [\eta_i(X)]^2} \quad \text{dans} \quad \overline{W}(\tau) \; \right|$$

$$s(t) = e^{at} \int_{t}^{+\infty} 2n\mu(\tau)e^{-a\tau} d\tau \quad \text{où} \quad 0 < a < 2(\lambda - \varrho).$$

On voit immédiatement que les fonctions $r(t)$, $\mu(t)$, $s(t)$, sont positives et tendent vers zéro lorsque $t \to +\infty$. Il existe donc un nombre T tel, que pour $t \geqslant T$ on a $s(t) < 1$, $\mu(t) < \dfrac{B + \lambda - \varrho}{2q}$, $r(t) < \dfrac{\delta}{\sqrt{2}}$, où δ a été défini dans le Lemme 1.

Soit ω l'ensemble défini par des inégalités

(ensemble ω) $\quad T < t, \; 0 < \sum_{i=1}^{q} x_i^2 < r^2(t), \quad \sum_{i=q+1}^{n} x_i^2 < s^2(t) \sum_{i=1}^{q} x_i^2.$

En vertu des propriétés des fonctions $r(t)$ et $s(t)$ il n'est pas difficile à démontrer que l'ensemble S des points de sortie de la frontière de l'ensemble ω coïncide avec l'ensemble des points de sortie stricte ([1] p. 292), et que la frontière de la sphère Z définie par des relations

(sphère Z) $\quad t = \tau, \; x_i = \xi_i \; (i = 1, \ldots, q), \quad \sum_{i=q+1}^{n} x_i^2 \leqslant s^2(\tau) \sum_{i=1}^{q} x_i^2$

où $\tau > t$ et $0 < \sum_{i=1}^{q} \xi_i^2 \leqslant r^2 < r^2(\tau)$, coïncide avec l'ensemble ZS. ZS n'est pas donc un rétracte de Z. D'autre part la transformation $(u, y_1, \ldots, y_n) = \Phi(t, x_1, \ldots, x_n)$ définie par des relations

$$u = \tau, \; y_i = \xi_i \; (i = 1, \ldots, q), \quad y_i = x_i \frac{s(\tau)}{s(t)} \sqrt{\frac{\sum_{\nu=1}^{q} \xi_\nu^2}{\sum_{\nu=1}^{q} x_\nu^2}} \quad (i = q+1, \ldots, n)$$

effectue la rétraction de S en SZ. En vertu du théorème de T. Ważewski ([1] p. 303) il existe un point $K \epsilon Z - S$ tel, que l'intégrale du système (3) issue du point K reste pour tous les $t \geqslant \tau$ dans l'ensemble ω.

Désignons par Q l'ensemble de tous les points K, que l'on obtient lorsque le point $(\xi_1, \ldots, \xi_q)$ varie dans le voisinage $v(\Theta, r)$ à q dimensions. L'ensemble Q est fermé (dépendance continue de l'intégrale de son point initial), tangent au plan N au point Θ (comme $s(t) \underset{t \to \infty}{\to} 0$) et situé dans l'ensemble U constituant le produit cartésien du voisinage $\sum\limits_{i=1}^{q} x_i^2 \leqslant r^2$ par le voisinage $\sum\limits_{i=q+1}^{n} x_i^2 \leqslant r^2$. Il en résulte que l'ensemble U est homéomorphe à une sphère fermée à n dimensions et que $Q \subset U \subset V(\Theta, \delta)$. En vertu du Lemme 1, l'ensemble Q est unifolié par rapport au plan N et par conséquent son équation peut être écrite sous la forme

(ensemble Q). $x_i = \Psi^{(i)}(x_1, \ldots, x_q)$ $(i = q+1, \ldots, n)$.

L'ensemble Q étant fermé, les fonctions $\Psi^{(i)}$ sont continues dans le voisinage fermé $v(\Theta, r)$ à q dimensions. On à $\Psi^{(i)}_{x_j}(\Theta) = 0$ car Q est tangent au plan N au point Θ.

L'existence du plan tangent à Q presque partout résultera d'un théorème de Rademacher lorsqu'on aura démontré que tous les quatre nombres dérivés de la fonction $\Psi^{(i)}(x_1, \ldots, x_q)$ $(i = q+1, \ldots, n)$ relatifs à chacune des variables x_i séparément sont bornés dans le voisinage $v(\Theta, r)$. La démonstration de cette propriété est tout à fait analogue à celle du Lemme 1.

R e m a r q u e 1. En appliquant un raisonnement analogue à celui du Lemme 1 on peut démontrer, dans certaines hypothèses concernant la régularité des fonctions $F^{(i)}$, que les fonctions $\Psi^{(i)}$ sont de classe C^1, C^2 etc.

R e m a r q u e 2. I. G. Petrowsky [2], dans un travail concernant un problème pareil, a traité exclusivement la question de la continuité de la surface Q. Afin de pouvoir appliquer la méthode des approximations successives il a préalablement soumis le système (3) à une transformation dépendant du temps t et des variables $y_1, \ldots, y_n$, transformation analogue, en un certain sens, à la transformation introduite par Bendixson [3] dans le cas $n = 2$ et ayant pour but la régularisation du problème. Notre méthode qui n'introduit pas les transformations auxiliaires de cette sorte est plus directe Elle permet en plus de démontrer que dans certaines hypothèses la surface Q est de classe de régularité C^1, C^2 etc., ce qui constitue le résultat essentiel de la note présente.

R e m a r q u e 3. En appliquant le Lemme 1 on peut obtenir les résultats du Théorème 1 au moyen de la méthode des approximations successives d'une façon simple et directe sans se servir d'une régularisation préalable.

R e m a r q u e 4. En remplaçant t par $-t$ on peut obtenir des résultats analogues pour l'ensemble R engendré par les trajectoires du système (1) tendant vers Θ lorsque $t \to -\infty$. En particulier il résulte de la Remarque 1 que dans les hypothèses convenables sur la régularité des fonctions $F^{(i)}$ le système 1 peut être transformé en un autre système de façon que les sur-

faces Q et R passent en surfaces planes Q^*, R^* situées respectivement sur le plan $\xi_{q+1} = \ldots = \xi_n = 0$ et sur le plan $\xi_1 = , \ldots \xi_q = 0$. Cette transformation permet de réduire l'étude plus detaillée de l'allure asymptotique des intégrales tendant vers l'origine au cas d'un système de la forme

$$d\,\xi_i/dt = \Phi^{(i)}(\xi_1, \ldots, \xi_q, 0, \ldots, 0) \quad (i = 1, \ldots, q)$$

ayant un noeud au point Θ.

Remarque 5. Martin [4] a étudié les surfaces Q et R dans l'hypothèse que les fonctions $F^{(i)}$ étaient analytiques c. à. d. dans le cas tout à fait différent du nôtre.

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On Satisfiability and Decidability
in Non-Classical Functional Calculi

by

H. RASIOWA and R. SIKORSKI

Communicated by K. KURATOWSKI at the meeting of March 16, 1953

Let S be a fixed consistent system of sentential calculus containing the disjunction sign $+$, the conjunction sign $\cdot$, and the implication sign $\rightarrow$. It is possible that S also contains other binary or unary sentential operators (e. g. the negation sign $-$, or the Lewis necessity sign $\square$). The rules of inference in S are: modus ponens and the rule of replacement of equivalent parts. We suppose that all the theorems of the positive sentential calculus [1, p. 422—450] are theorems of S.

The system S determines in an obvious way a system S^* of functional calculus with individual variables $x_1, x_2, \ldots$, with k-argument functional variables $F_1^k, F_2^k, \ldots$ ($k = 1, 2, \ldots$), and with the quantifiers $\underset{x_i}{\Sigma}, \underset{x_j}{\Pi}$. The rules of inference in S^* are modus ponens, the rule of replacement of equivalent parts, the rule of substitution for individual variables, and the four known rules for quantifiers. The theorems in S^* are all substitutions of theorems of S and all their consequences.

The system S determines uniquely a kind of abstract algebras (called S-algebras) with algebraical operations corresponding to the logical sentential operators $+, \cdot, \rightarrow, \ldots$ The S-algebras, which are the matrices of the system S, are relatively pseudocomplemented lattices (with the sum (join) $a + b$ and the product (meet) $a \cdot b$) having the unit element e which is the distinguished element corresponding to the logical value of truth. If an S-algebra is a complete lattice, it is called an S^*-algebra. We shall suppose that the S-algebras A have the property: given an enumerable set of infinite sums and products in A, $a_n = \underset{i}{\Sigma} a_{n,i}, b_n = \underset{i}{\Pi} b_{n,i}$, there is an isomorphism (with respect to all the operations $+, \cdot, \rightarrow, \ldots$) of A into an S^*-algebra which preserves all these sums and products.

For instance, if $S_\alpha (S_\lambda, S_\chi, S_\pi)$, is the classical (Lewis [*]), Heyting, posi-

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[*]) The Lewis system S_4 — see Lewis and Langford [3]. Notice that, in our paper the implication $\rightarrow$ is the usual implication (not the Lewis strict implication).

tive) sentential calculus then S_x^* ($S_\lambda^*, S_\chi^*, S_\pi^*$ *) is the classical (Lewis, Heyting, positive) functional calculus, and S_x-algebras (S_λ-, S_χ-, S_π-algebras) are Boolean algebras (closure algebras, relatively pseudocomplemented lattices with the zero element **), relatively pseudocomplemented lattices).

Let J be a non-empty set, and let A be an S^*-algebra. Following Mostowski, each formula $\alpha \epsilon S^*$ can be interpreted as an algebraical functional $(J, A) \Phi_\alpha$ if we interpret the individual variables as variables running over J, the functional variables F_m^k — as variables running over the set of all mappings of $\underbrace{J \times J \times \ldots \times J}_{k\text{-times}}$ into A, and logical signs — as the signs of the corresponding algebraical operations, in particular the quantifiers Σ and Π as the infinite sums and products.

A set $R \subset S^*$ is said to be satisfiable in a set $J \neq 0$ and in an S^*-algebra A if all the functionals $(J, A) \Phi_\alpha$ ($\alpha \epsilon R$) assume the value $e \epsilon A$ for a common (independent of α) substitution for the variables x_i, F_m^k ($i, k, m = 1, 2, \ldots$). R is said to be satisfiable in J if it is satisfiable in J and in an S^*-algebra A. R is satisfiable if it is satisfiable in a set $J \neq 0$.

A formula $\alpha \epsilon S^*$ is said to be valid if $(J, A) \Phi_\alpha = e \epsilon A$ identically for every set $J \neq 0$ and for every S^*-algebra A.

In the case of the classical functional calculi S_x^* the above definitions of satisfiability and validity are equivalent to the known definitions of Tarski.

Let I denote the set of all positive integers.

Theorem I.***) *A formula α is provable in S^* if and only if α is valid (or: if α is valid in the set I, i. e. if $(I, A) \Phi = e \epsilon A$ identically for each S^*-algebra A). Each consistent set $R \subset S^*$ is satisfiable in the set I.*

Theorem II. *If the system S contains the negation sign and if the formula $(-(\sigma \to \sigma_i) \to \tau$ is a theorem in S, then each satisfiable set $R \subset S^*$ having the deduction property ****) is consistent and satisfiable in the set I.*

If X is a topological space ([2], p. 37), then $C(X)$ ($H(X)$) denotes the class of all subsets (of all open subsets) of X. $C(X)$ is an S_λ^*-algebra (with the usual operations $a + b$, $a \cdot b$, and $a \to b = (X - a) + b$, $-a = X - a$, $\square\, a =$ the interior of a), and $H(X)$ is an S_χ^*-algebra and S_π^*-algebra (with the usual operations $a + b$, $a \cdot b$, and $a \to b =$ the interior of $((X - a) + b)$, $- a = a \to 0$).

Theorem III. *There is a topological space X such that*

(i) *a formula $\alpha \in S_\lambda^* (S_\chi^*, S_\pi^*)$ is provable if and only if $(I, C(X)) \, \Phi_\alpha = X$ $((I, H(X)) \, \Phi_\alpha = X)$ identically;*

(ii) *a set $R \subset S_\lambda^* (S_\chi^*, S_\pi^*)$ having the deduction property is satisfiable if and only if it is satisfiable in I and in $C(X)$ $(H(X))$.*

It follows from Theorem III (i) that:

Theorem IV. *A formula $\alpha \in S_\pi^* (S_\chi^*)$ is provable in $S_\pi^* (S_\chi^*)$ if and only if it is provable in S_λ^* (in S_λ^* provided that the expressions $\beta \rightarrow \gamma$, $- \beta$, $\Pi \beta$ of S_χ^* are interpreted in S_λ^* as $\square\,(\beta \rightarrow \gamma)$, $\square\,(-\beta)$, $\square\,\Pi\,\beta$ respectively).*
$$\scriptstyle x_i \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad x_i$$

Theorem V. *Let $\alpha, \beta \in S_\lambda^* (S_\chi^*, S_\pi^*)$. If $\square\,\alpha + \square\,\beta$ $(\alpha + \beta)$ is provable in S_λ^* (in S_χ^*, in S_π^*), then either α or β is provable in $S_\lambda^* (S_\chi^*, S_\pi^*)$ *). If $\Sigma_{x_i} \square\,\alpha$ $(\Sigma_{x_i}\,\alpha)$ is provable in $S_\lambda^* (S_\chi^*, S_\pi^*)$ then there is an integer q such that the substitution $\alpha \binom{x_q}{x_i}$ is provable in $S_\lambda^* (S_\chi^*, S_\pi^*)$.*

Theorem VI. *Each formula $\beta \in S_\lambda^* (S_\chi^*, S_\pi^*)$ of the form $\beta = \Xi\,\alpha$, where α contains no quantifier and Ξ is a sequence of the signs $\Sigma_{x_i} \square$, Π_{x_j} (of the signs Σ_{x_i} and Π_{x_j}), is decidable **).*

Similar theorems also hold for the minimal functional calculus S_μ^* determined by the minimal sentential calculus S_μ.

Institute of Mathematics, Polish Academy of Sciences

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*) An analogous theorem for the sentential calculus of Heyting was obtained by K. Gödel [5].

) Complete proofs of Theorems I—VI may be found in Fundamenta Mathematicae **40 (1953) and **41** (1954).

Solution d'un problème d'Urysohn concernant les espaces métriques universels

par

S. MRÓWKA

Présenté par K. KURATOWSKI à la séance du 18 Mai 1953

L'espace U d'Urysohn [1], [2] jouit des propriétés suivantes:

1. l'espace U est universel par rapport aux espaces métriques séparables, c'est-à-dire que, pour tout espace métrique séparable X, il existe une transformation isométrique de X en sous-ensemble de U.

2. l'espace U est séparable,

3. l'espace U est homogène par rapport aux ensembles finis, c'est-à-dire qu'à tout couple d'ensembles isométriques finis A et B, contenus dans U, correspond une transformation isométrique de l'espace U en lui-même, qui transforme A en B.

Urysohn, qui a établi les propriétés 1—3 de l'espace U, a posé le problème suivant: *l'espace U est-il homogène par rapport aux ensembles dénombrables?*

Nous nous proposons de démontrer dans cette note que la réponse à cette question est *négative*. Elle résulte du théorème général suivant que nous allons établir:

T h é o r è m e. *Tout espace métrique E, universel par rapport aux espaces métriques dénombrables et homogène par rapport aux sous-ensembles dénombrables, est non séparable.*

D é m o n s t r a t i o n. Il suffit évidemment de démontrer que l'espace E contient un sous-ensemble F de puissance $\aleph_1$ dont tout couple de points x, y satisfait à la condition:

(1) $$\text{si} \quad x \neq y, \quad \text{on a} \quad |x - y| = 1.$$

Nous définissons à cet effet par l'induction transfinie une suite de sous-ensembles de E:

$$A_\omega, A_{\omega+1}, \ldots, A_\alpha \ldots \qquad (\alpha < \Omega)$$

tels que, pour tout α

(2) $$A_\beta \subset A_\alpha \neq A_\beta \quad (\beta < \alpha)$$

[233]

et que chaque couple de points x, y de A_α satisfait à la condition (1); nous posons ensuite

$$F = \sum_{\omega \leqslant \alpha < \Omega} A_\alpha.$$

Pour A_ω nous prenons un sous-ensemble arbitraire de puissance $\aleph_0$ de E qui satisfait à la condition (1).

Pour $\alpha > \omega$ (fixe), admettons que tous les ensembles A_ξ avec $\omega \leqslant \xi < \alpha$ sont de puissance $\aleph_0$ et satisfont aux conditions (1) et (2). En posant

$$S_\alpha = \sum_{\omega \leqslant \xi < \alpha} A_\xi,$$

l'ensemble S_α satisfait aussi à la condition (1).

Soit p_α un point arbitraire de S_α et soit $T_\alpha = S_\alpha - \{p_\alpha\}$. Les deux ensembles T_α et S_α sont donc de puissance $\aleph_0$ et satisfont à la condition (1); il sont, par conséquent, isométriques (évidemment, toute transformation biunivoque de T_α en S_α est une isométrie). Il existe donc une isométrie f de l'espace E en lui-même telle que $f(T_\alpha) = S_\alpha$. Posons $A_\alpha = S_\alpha + f(p_\alpha)$.

Pour tout $x \in T_\alpha$ on a $|x - p_\alpha| = 1$, d'où $|f(x) - f(p_\alpha)| = 1$, donc $|y - f(p_\alpha)| = 1$ pour tout $y \in S_\alpha$. Cela veut dire que l'ensemble A_α satisfait à la condition (1) et que $S_\alpha \subset A_\alpha \neq S_\alpha$.

Il en résulte que l'ensemble F vérifie la condition (1) et qu'il est de la puissance $\aleph_1$.

Remarque 1. Un raisonnement analogue permet de généraliser notre théorème de la façon suivante:

Tout espace métrique universel par rapport aux espaces métriques de puissance $< \aleph_\xi$ et homogène par rapport aux sous-ensembles de puissance $< \aleph_\xi$ contient un ensemble de puissance $\aleph_\xi$ satisfaisant à la condition (1).

Remarque 2. Remplaçons l'hypothèse d'homogénéité de l'espace E relative aux ensembles dénombrables par la suivante: toute isométrie entre deux sous-ensembles dénombrables de E se laisse étendre à une isométrie de l'espace tout entier en lui-même. On peut démontrer que, dans cette hypothèse, l'espace E est universel par rapport aux espaces métriques de puissance $\aleph_1$. D'une façon plus générale:

Étant donné un espace métrique X universel par rapport aux espaces métriques de puissance $< \aleph_\xi$, l'hypothèse que toute isométrie entre des sous-ensembles de puissance $< \aleph_\xi$ de X se laisse étendre en une isométrie de l'espace X en lui-même, implique que cet espace est universel par rapport aux espaces métriques de puissance $\aleph_\xi$.

Institut Mathématique de l'Académie Polonaise des Sciences

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The Limiting Distributions of Sums of Arbitrary Independent and Equally Distributed r-point (r ⩾ 2) Random Variables

by

M. FISZ

Communicated by H. STEINHAUS at the meeting of April 23, 1953

1. We consider a sequence $X_n(n = 1, 2, \ldots)$ of random variables, where X_n is for each n a sum of n independent and equally distributed r-point $(r \geqslant 2)$ random variables $Y_{nk}(k = 1, 2, \ldots, n)$.

Let A_n and $B_n \neq 0$ be sequences of constants and let the sequence $F_n(z)$ of distribution functions of the random variables ζ_n defined by the formula

$$\zeta_n = \frac{X_n}{B_n} - A_n$$

converge as $n \to \infty$ to a distribution function $F(z)$. We can ask: What limiting distribution functions $F(z)$ are possible? The answer to this question is given by theorems 2.1—2.3. On the other hand in theorems 3.1—3.2 we specify the sequences A_n and B_n and find — in some cases — sufficient conditions for the convergence of the sequences of distribution functions $F_n(z)$ to a given distribution function $F(z)$.

We give the theorems mentioned without proofs. In a paper to be published in "Studia Mathematica" 14, 1 the proofs will be given.

2. Theorem 2.1. Let $X_n(n = 1, 2, \ldots,)$ be a sequence of sums of random variables

$$(2.1) \qquad X_n = \sum_{k=1}^{n} Y_{nk}$$

and let the random variables $Y_{nk}(k = 1, 2, \ldots, n)$ be for each n independent and equally distributed according to the distribution law

$$(2.2) \qquad P(Y_{nk} = a_{nl}) = p_{nl} \qquad (l = 1, 2, \ldots, r)$$

where $r \geqslant 2$ and a_{nl} and p_{nl} are arbitrary functions of n and where $0 \leqslant p_{nl} \leqslant 1$, $\sum_{l=1}^{r} p_{nl} = 1$. If for some sequences of constants A_n and $B_n \neq 0$

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the sequence $F_n(z)$ of distribution functions of the variables

$$(2.3) \qquad \zeta_n = \frac{X_n}{B_n} - A_n$$

converges as $n \to \infty$ to a non-singular distribution function $F(z)$, then $F(z)$ is necessarily a distribution function of a sum of independent variables namely of $s(0 \leqslant s \leqslant r\text{-}2)$ Poisson variables *) and $v(v = 0 \text{ or } 1)$ normal variables or of a sum of $r\text{-}1$ Poisson variables.

From theorem 2.1 it follows immediately that when $r = 2$, the function $F(z)$ will necessarily be a distribution function of a normal variable or of a Poisson variable. A special case of this consequence of theorem 2.1, when $a_{n1} = a_1$ and $a_{n2} = a_2$ are constants independent of n, was given by Kozuliayev [1].

We shall give here some other interesting special cases of theorem 2.1.

T h e o r e m 2.2. If in theorem 2.1 the formula (2.2) is of the form

$$(2.4) \qquad P(Y_{nk} = a_l) = p_{nl} \qquad (l = 1, 2, \ldots, r)$$

where $a_{l_1} \neq a_{l_2}$ when $l_1 \neq l_2$ then the numbers s and v in the conclusion of theorem 2.1 cannot both be different from 0.

Thus if the $a_{nl} = a_l$ are for each n and l independent of n, then the limiting non-singular distribution function $F(z)$ is necessarily a distribution function of a normal variable or of a sum of s Poisson variables, where $1 \leqslant s \leqslant r\text{-}1$.

T h e o r e m 2.3. If in theorem 2.1, the formula (2.2) is of the form:

$$(2.5) \qquad P(Y_{nk} = a_{nl}) = p_l \qquad (l = 1, 2, \ldots, r)$$

where $p_l \neq 0$, then the conclusion of theorem 2.1 will be $s = 0$ and $v = 1$.

Thus if for each n and l we have $p_{nl} = p_l$ where $p_l \neq 0$ the function $F(z)$ will be a distribution function of a normal variable.

3. T h e o r e m 3.1. Let X_n be a sequence of sums of random variables

$$X = \sum_{k=1}^{n} Y_{nk}$$

where the random variables Y_{nk} are for each n independent and equally distributed according to the distribution law

$$(3.1) \qquad \begin{aligned} P(Y_{nk} = a_1) &= p_{n1} \\ P(Y_{nk} = a_{n2}) &= p_{n2} = 1 - p_{n1} \end{aligned}$$

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*) We say, that the random variable Y is a Poisson variable if for each $j = 0, 1, \ldots$ the following equality holds

$$P(Y = aj + b) = \frac{e^{-\lambda}\lambda^j}{j!}$$

where $a \neq 0$, $\lambda > 0$ and b are constants.

and where a_{n1}, a_{n2}, and p_{n1} are arbitrary functions of n. Let $F_n(z)$ be the sequence of distribution functions of the standardized random variables

$$(3.2) \qquad \zeta_n = \frac{X_n - E(X_n)}{\sqrt{D(X_n)}}.$$

Then:

a. If the following relation holds

$$(3.3) \qquad \lim_{n \to \infty} n p_{n1}(1 - p_{n1}) = + \infty$$

the sequence $F_n(z)$ will satisfy the relation

$$(3.4) \qquad \lim_{n \to \infty} F(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-\frac{t^2}{2}} dt.$$

b. If the following relations hold

$$(3.5) \qquad \lim_{n \to \infty} p_{n1} = p_1$$

$$(3.6) \qquad \lim_{n \to \infty} n p_{n1}(1 - p_{n1}) = \lambda$$

where $0 < \lambda < \infty$ and if there exists an integer n_0 such that for $n > n_0$ all the differences $a_{n1} - a_{n2}$ have the same sign, then $F_n(z)$ converges when $n \to \infty$ to a distribution function $F(z)$ of a Poisson variable (in all continuity points of $F(z)$).

Theorem 3.2. Let X_n be a sequence of random variables defined by

$$X_n = \sum_{k=1}^{n} Y_{nk}$$

where the random variables Y_{nk} are for each n and $k = 1, 2, \ldots, n$ independent and equally distributed according to the law

$$(3.7) \qquad P(Y_{nk} = a_l) = p_{nl}$$

and where $0 \leqslant p_{n1} \leqslant 1$, $\sum_{l=1}^{r} p_{nl} = 1$. Let $F_n(z)$ be the sequence of distribution functions of the random variables defined by the formula (3.2). Then:

a. If the following relation holds

$$(3.8) \qquad \lim_{n \to \infty} n[p_{n1}p_{n2} + p_{n1}p_{n3} + , \ldots, + p_{n(r-1)}p_{nr}] = + \infty$$

the sequence $F_n(z)$ will satisfy the relation

$$(3.9) \qquad \lim_{n \to \infty} F(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-\frac{t^2}{2}} dt.$$

b. If the following relation holds

$$(3.10) \qquad \left. \begin{aligned} \lim_{n\to\infty} p_{nl} &= p_l \\ \lim_{n\to\infty} n p_{nl} &= \lambda_l \end{aligned} \right\} \; l = 1, 2, \ldots, r$$

$$(3.12) \qquad \lim_{n\to\infty} n[p_{n1} p_{n2} + p_{n1} p_{n3} + , \ldots, + p_{n(r-1)} p_{nr}] = \lambda,$$

where $0 < \lambda < \infty$, then the sequence $F_n(z)$ converges when $n \to \infty$ to a distribution function $F(z)$ of a sum of s Poisson variables where $1 \leqslant s \leqslant r - 1$ (in all continuity points of $F(z)$).

Institute of Mathematics, Polish Academy of Sciences

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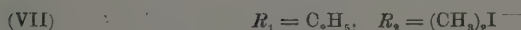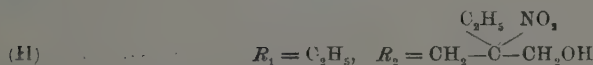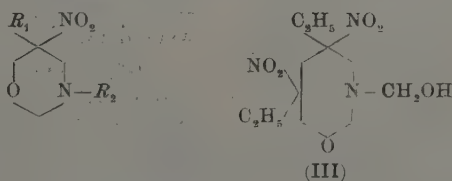# On the Structure of Some Aliphatic Nitro-Compounds

by

T. URBAŃSKI

Communicated at the meeting of April 20, 1953

As I have indicated earlier, the reaction of nitroparaffins with formaldehyde and ammonia or amines may lead to the formation of polymers [1]. Further experiments [2] have shown that a number of new ring compounds of 1,3-tetrahydrooxazine (I and II) and 1-oxa-3-aza-cyclooctane (III) type were formed by the interaction of 1-nitropropane with formaldehyde and ammonia. The products can be transformed into hydrochlorides of the open chain amines (IV), (V), (VI), or into methyliodide (VII). 2-Nitropropane yielded the amine (VIII) [3] with formaldehyde and ammonia.

More recently, my co-workers and I isolated the compounds (IX) and (X) from nitroethane, formaldehyde and ammonia reaction products [4]. A tetrahydrooxazine derivative (XI) was also prepared from 1-nitropropane, formaldehyde and methylamine [5].
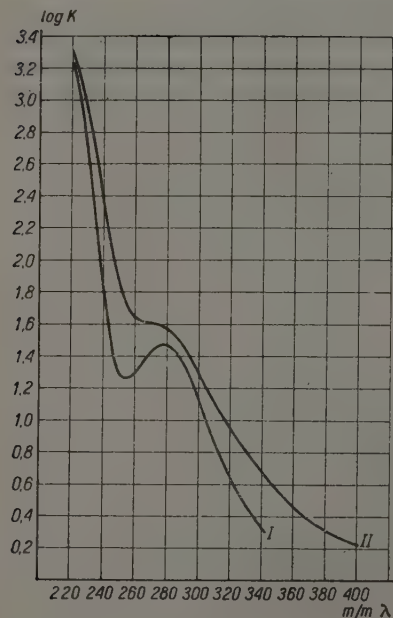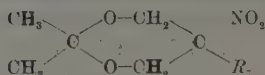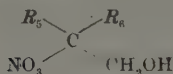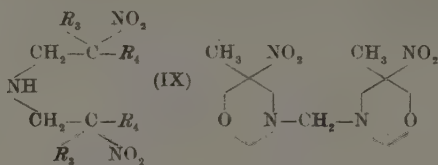

(I) $\quad R_1 = C_2H_5, \quad R_2 = H$

(II) $\quad R_1 = C_2H_5, \quad R_2 = CH_2-\overset{\displaystyle C_2H_5}{\underset{\displaystyle NO_2}{C}}-CH_2OH$

(VII) $\quad R_1 = C_2H_5, \quad R_2 = (CH_3)_2I^-$

(XI) $\quad R_1 = C_2H_5, \quad R_2 = CH_3$

(V)

$$CH_2-\overset{C_2H_5}{\underset{}{C}}\overset{NO_2}{}-CH_2-\overset{C_2H_5}{\underset{}{C}}\overset{NO_2}{}-CH_2OH$$

$$\begin{array}{cc} R_3 & NO_2 \\ CH_2{-}C{-}R_4 \\ NH \qquad (IX) \\ CH_2{-}C{-}R_4 \\ R_3 & NO_2 \end{array}$$

$$\begin{array}{cc} CH_3 & NO_2 \\ \end{array} \qquad \begin{array}{cc} CH_3 & NO_2 \end{array}$$

$$O \quad N{-}CH_2{-}N \quad O$$

(IV) $R_3 = C_2H_5, \quad R_4 = CH_2OH$

(VIII) $R_3 = CH_3, \quad R_4 = CH_3$

(X) $R_3 = CH_3, \quad R_4 = CH_2OH$

$$\begin{array}{cc} R_5 & R_6 \\ C \\ NO_2 & CH_2OH \end{array}$$

(VI) $R_5 = C_2H_5, \quad R_6 = CH_2NH_2$

(XII) $R_5 = CH_3, \quad R_6 = CH_2OH$

(XIII) $R_5 = C_2H_5, \quad R_6 = CH_2OH$

(XIV) $R_5 = CH_3, \quad R_6 = CH_3$

$$\begin{array}{cc} CH_3 & O{-}CH_2 \qquad NO_2 \\ C \qquad\qquad C \\ CH_3 & O{-}CH_2 \qquad R_7 \end{array}$$

(XV) $R_7 = CH_3$

(XVI) $R_7 = CH_2OH$

Fig. 1

The ultra-violet absorption spectra of all these products and also of nitroparaffins, the ketals [6] and a series of known nitroalcohols (XII–XIV) deriving from nitroparaffins were determined.

Experiments with the spectrophotometer were carried out by Mrs. J. Świętosławska-Ściślowska and Miss D. Ciecierska at the Institute of General Chemistry, Warsaw.

Two types of absorption curve were found:

.I. One with a maximum in the proximity of $\lambda = 270$ mμ, which corresponds to the absorption typical for the nitro-group;

II. The other with a bend in the proximity of $\lambda = 270$ mμ.

The shapes of typical curves are shown in Fig. 1. The results of the experiments are tabulated below.

Substance	Solvent	Maximum (curve I)	Bend (curve II)
Nitromethane, Nitroethane, 2-Nitropropane	Ethyl alcohol	260 mμ	—
1-Nitropropane	,, ,,	270 mμ	—
(XV)	,, ,,	280 mμ	—
(XVI)	,, ,,	284 mμ	—
(VIII), (base)	,, ,,	260 mμ	—
(II), (III), (bases)	,, ,,	260 mμ	—
(IX), (base)	,, ,,	262 mμ	—
(XIV)	Water	280 mμ	—
(I) hydrochloride	,,	270—272 mμ	—
(XI) hydrochloride	,,	270 mμ	—
(VII) iodide	,,	275 mμ (weak)	—
(XII), (XIII)	,,	—	ca. 265 mμ
(IV), (V), (VI), (VIII), (X), hydrochlorides	,,	—	260—280 mμ
(X), (base)	Ethyl alcohol	—	260 mμ (strong)

The following conclusions can be deduced from these results:

1. No maximum is observed, if two hydroxyl-groups [e. g. in (XIII)] can form two six member rings with both oxygen atoms of the nitro-group (XIII a):
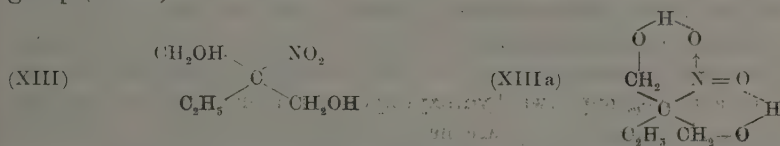
The slight bend of the absorption-curve is produced either by equilibrium between the two forms (XIII) and (XIII a) or by weak action of the nitro-group in (XIII a). One hydroxyl-group is not sufficient to suppress the absorption bend of the nitro-group (compound XIV).

2. No maximum is observed if an amino-group with hydrogen atoms [e. g. in (VIII)] hydrochloride can form six-member rings in such a way, that one N-hydrogen atom forms a bond with one of the oxygen atoms of the nitro-group as in (VIII a) hydrochloride:

(VIII a)

$$CH_3 \quad \overset{\overset{O}{\uparrow}}{N} = O$$
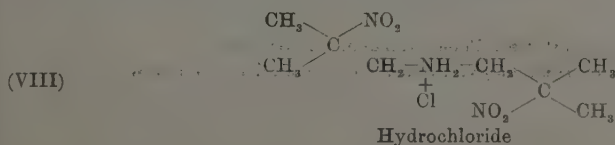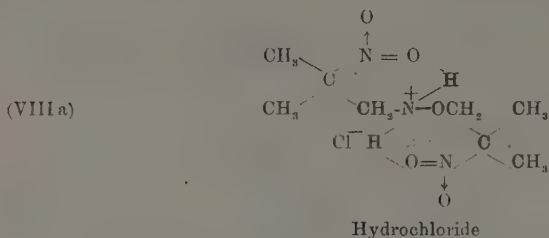
Hydrochloride

3. If in addition to the amino-group the hydroxyl-groups are also present [(IV), (V), (VI) and (X)], the bend in the case of the hydrochlorides is very insignificant, probably owing to the formation of hydrogen bonds through both the amino- and hydroxyl-groups.

That is probably the reason why free bases [(IV), (V) and (X)] do not give a maximum:

(X)

(Free base)
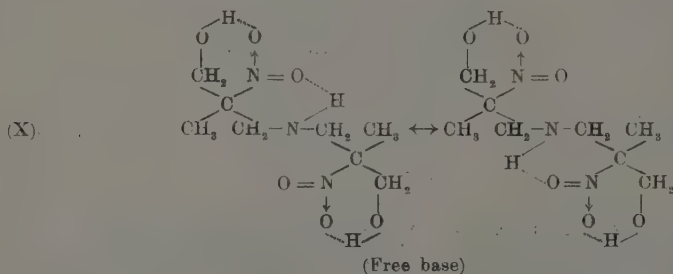
By means of atomic models it has been found that the distance between the hydrogen atoms of the hydroxyl or amino-groups and the oxygen atoms of the nitro-group is sufficiently small to assure the existence of hydrogen bonds.

It remains unexplained, why, in order to suppress the absorption maximum of a nitro-group, two hydroxyl-hydrogen atoms and only one hydrogen atom of an amino-group are necessary. This may be due to the strong electron-repelling property of the amino-group combined with the electron attracting property of the nitro-group.

It is interesting to note that in some instances a chelate six-member ring through an OH and NO_2 group was earlier postulated by S. Malinowski and the author [6], on the basis of the chemical properties of a nitrodiol.

The author is much indebted to Mrs. J. Świętosławska-Ścisłowska and to Miss D. Ciecierska for supplying the results of spectrophotometer-measurements.

Organic Chemistry Laboratories, Polish Academy of Sciences
Department of Organic Technology, Institute of Technology, Warsaw

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Electrometric Adsorption Analysis of the Alkaloids of the Poison Nut (Strychnos Nux vomica) on Aluminium Oxide. Potentiometric Chromatography

by

B. KAMIEŃSKI and B. WALIGÓRA

Communicated by B. KAMIEŃSKI at the meeting of March 16, 1953

Several papers (see References [1]−[9] at the end of this paper) have been published on the application of a special type of microelectrode to the elute flowing out of an adsorption tube. Very dilute solutions of acids, bases, reducing or metallic ions may be indicated by an antimony, platinum or other microelectrode, put into contact with drops of the elute.

Very pure adsorbents should be used in this sensitive method. Commercial aluminium oxide prepared for chromatographic purposes (Brockmann) is not pure enough. Consequently, a portion of commercial aluminium oxide weighing 250 g was washed for 45 days; 75 litres of distilled water were necessary for this purpose. Thus, by decanting the distilled water and changing it every day, a sufficiently pure oxide was obtained. The oxide was dried and used for the electrometric adsorption analysis of extracts of the Poison Nut.

An antimony microelectrode of suitable construction (see References) was put into contact with the drops flowing out of the adsorption tube and the potential was measured and plotted against the volume of the elute.

The following solutions were analysed with the aid of this electrode:

1. An extract (D. A. B. VI) containing 12·9 mg of dry substances in 1 ml of solution.

2. A degreased extract containing 14·4 mg of dry substances in 1 ml of solution.

3. Alkaloids separated by the adsorption analysis, containing 11·8 mg of dry substances in 1 ml of solution.

The frontal analysis of the extract (D. A. B. VI) of Nux vomica is represented in Fig. 1. A volume of 4 ml of the extract was diluted to 40 ml with 70°/₀ ethanol and poured onto the top of the column. An aluminium
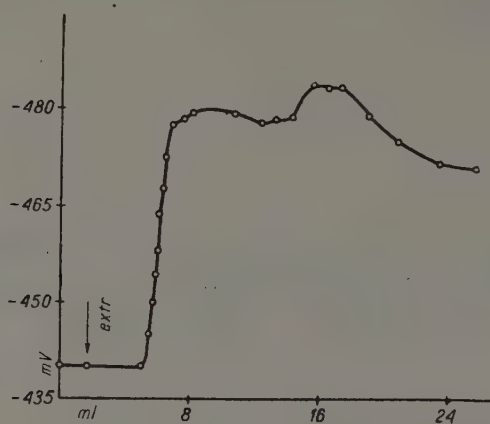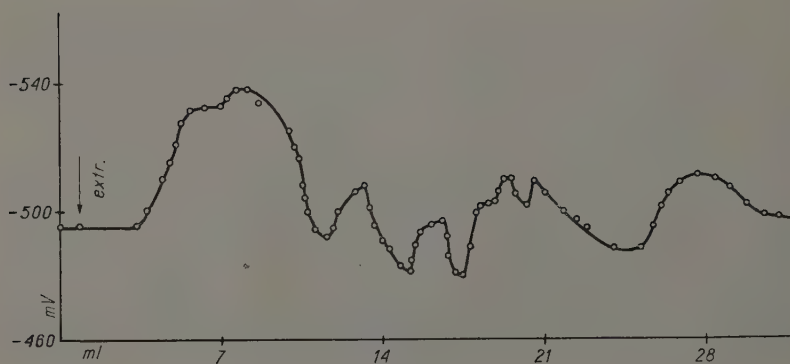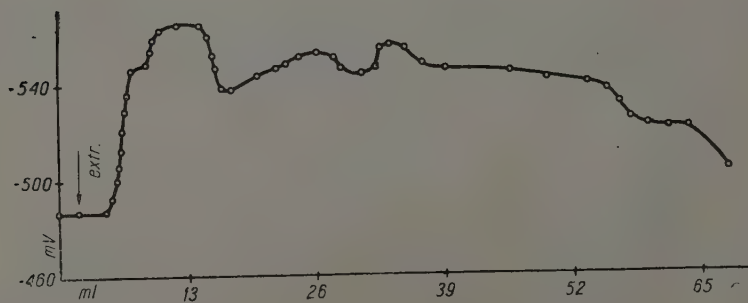
Fig. 1

Fig. 2

Fig. 3

oxide column 100 mm high and 7 mm in diameter was used. When a volume of 17 ml of the eluent reached the bottom and wetted the microelectrode which had been placed in such a way as to contact the drops flowing out of the column, changes in the potential became visible. A volume of about 3·5 ml of the eluent passed the microelectrode without any change in the potential. The experiment lasted 41 minutes. Acid substances appeared at the end of the experiment. It may thus be concluded that aluminium oxide adsorbs acids very strongly so that in the end they are eluted.
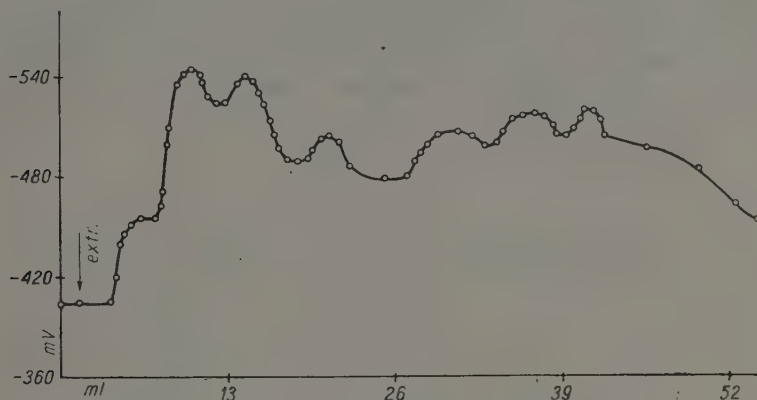

Fig. 4

The object of our next experiments was to obtain an analysis of the extract (Fig. 2). The column used was somewhat higher (150 mm), and 5 ml of the extract, which contained 64·5 mg of dry substance, were poured on to the top of the column. Analytical tests applied to the first 7 ml (first step of the potential) proved that only brucine was present. The following 4 ml (next step of the potential) contained strychnine only. A 70% solution of ethanol was the eluent used and the experiment lasted 94 minutes. Several changes in the potential followed: these were due to the presence of the other alkaloids and to the acid substances which are frequently associated with alkaloids.

A more precise separation of the alkaloids was obtained when a de-greased extract was applied. Ground nuts (Strychnos Nux vomica) were degreased with benzine (B. P. 45° to 55° C) and an extract was prepared. 4 ml of this extract, which contained 57·6 mg of dry substances, were poured on the top of the column (100 mm high, 7 mm in diameter). Ethanol (70%) was applied as an eluent (Fig. 3). The first change in the potential is due to brucine, the next to strychnine, as may easily be seen when analytical tests are applied to the dry substance of the elution. The next maxima are due to other more strongly adsorbed alkaloids. The experiment lasted 135 mi-

nutes. It is worth noting that a second adsorption analysis applied to a part of the elution (a fraction) results in sharper maxima and eventually reveals a greater number of substances. In order to check this supposition a volume of 63 ml from the experiment shown in Fig. 3 was condensed to 1 ml by evaporation, diluted to 3 ml with a 94% ethanol solution and poured on
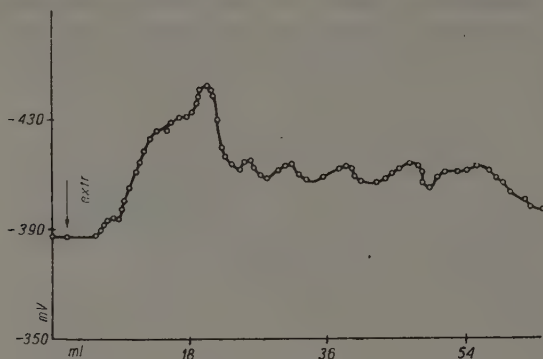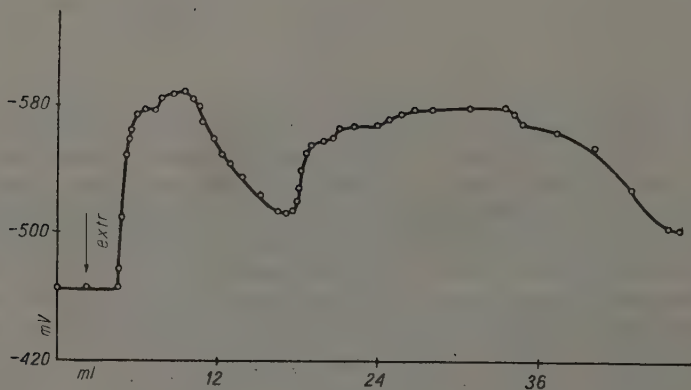

Fig. 5

Fig. 6

the top of a similar column (100 mm high). The column was eluted with a 70% solution of ethanol. Here (Fig. 4) a greater number (7) of steps and maxima were observed. These were due to the appearance of further alkaloids analysed by adsorption for the second time. The experiment lasted 123 minutes.

The potential of the electrode is approximately proportional to the logarithm of the concentration (see References). In other words, a large

decrease in the strength of the concentration is accompanied by a small change in the potential. Consequently, the electrometric method may be applied to very diluted solutions. Taking into account the fact that the greater the dilution the better the separation on the columns, it was to be expected that more steps and maxima would appear if more diluted solutions were applied, and yet the potential changes would be great enough to be observed with sufficient accuracy.

The extract was diluted 10 times and in another experiment 100 times and analysed. Fig. 5 represents the results of dilution ×100. A quantity (4 ml in volume) of an extract containing 0·576 mg of dry substances was poured on the top of a column 100 mm high and eluted with a 70% solution of ethanol. There are signs of at least 8 maxima and steps, on the curve, against 7 in Fig. 4.
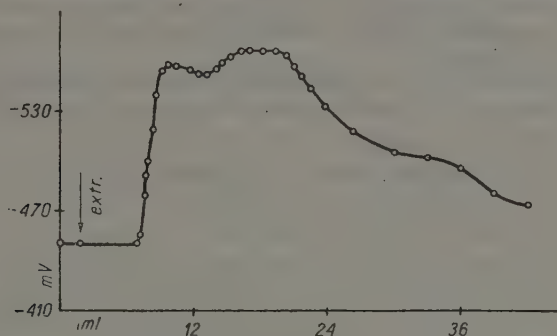

Fig. 7

It is clear from the above results that separation is much better when the adsorption analysis is applied more often to a suitable fraction of the elution.

Since we are concerned with dilute solutions, a volume of 1 ml of degreased alkaloids, (D. A. B. VI. 234, 1938) containing 11.8 mg of dry substances, was poured on the top of a column of pure aluminium oxide (100 mm high). Fig. 6 represents the change in the potential when a 70% ethanol solution was applied as eluent. The experiment lasted 58 minutes.

Lastly (Fig. 7), the fraction containing the brucine and strychnine of experiment 6 (14 ml) was condensed by evaporation to 1 ml, the solution diluted to 3 ml with 94% ethanol and put again on the top of the column (200 mm high). 70% ethanol was applied as eluent.

The separation of brucine and strychnine was much more effective. The experiment lasted 100 minutes. It should be emphasized that a slight minimum between the two maxima denotes a very good separation owing to the logarithmic character of the potential function.

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[8] K a m i e ń s k i B., B y ł o Z., W a l i g ó r a B., *Properties of the Antimony Microelectrode in Aqueous Alcoholic Solutions.* Potentiometric Chromatogrophy, this volume, Nos 3—4, 137—141.

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Electrometric Adsorption Analysis of the Alkaloids
of the Poison Nut (Strychnos Nux vomica) on Charcoal.
Potentiometric Chromatography

by

B. KAMIEŃSKI and Z. BYŁO

Communicated by B. KAMIEŃSKI at the meeting of March 16, 1953

Charcoal is one of the most useful adsorbents. Its colour, however, is an impediment to its adaptability to chromatographic analysis. Nevertheless some modern methods of chromatographic analysis, such as e. g. the Tiselius method or the potentiometric method, allow the use of charcoal without restriction, provided that the charcoal is of the purest quality.

In the experiments about to be described Merck's charcoal was used. It is acid, and when a small portion of it (1 g in 100 ml water) was put into distilled water a rising degree of acidity was observed until a pH 5·2 was reached. The grain of the charcoal used was from 0·08 to 0·12 mm in diameter. It is impossible to apply this excellent adsorbent without thoroughly purifying it. It took 33 days to prepare 100 g of charcoal for potentiometric chromatography by purifying it with water and ethanol. The distilled water was changed twice every day, and 120 l of water were needed in all. Lastly, ethanol of the purest quality was applied and the adsorbent dried for 150 minutes at 110° C.

Charcoal columns of 7 mm diameter and of different heights, mostly from 20 mm to 100 mm, were used. An antimony microelectrode (see References [1] to [9] at the end of this paper) was put into contact with the drops flowing out of the tube, and the potential of the antimony microelectrode was checked against the volume of the eluent flowing out of the tube.

First of all the behaviour of the adsorbent was investigated by means of the application of artificial mixtures of strychnine and brucine. A mixture of 39·4 mg brucine and 33·4 mg strychnine dissolved in 60 ml of a 70% solution of ethanol was prepared and poured slowly onto the top of a charcoal column 20 mm high. The results are shown in Fig. 1. The experiment lasted 41 minutes. The course of the curve is typical for a fron-

18*

tal analysis. Observation of the chemical reactions and electro-chemical behaviour led to the discovery that brucine is the first to appear in the elution. By doubling the height of the column of charcoal to 40 mm and applying the same solution, it was possible to observe small changes in the
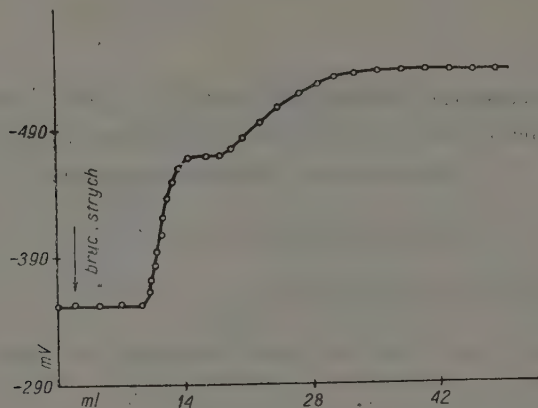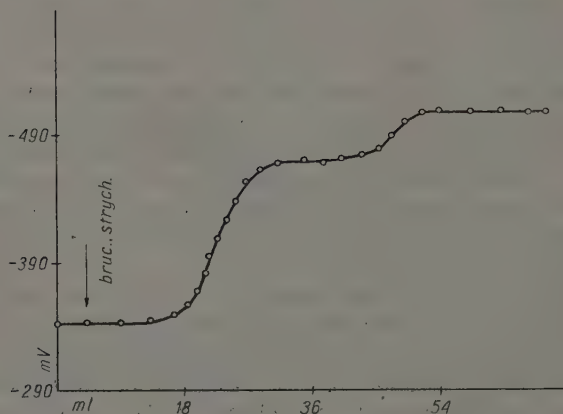

Fig. 1

Fig. 2

course of the curve (see Fig. 2). This second experiment lasted 58 minutes. The third experiment (Fig. 3) shows the results of a change in the ratio of brucine to strychnine. This time 15·7 mg of brucine and 30·4 mg of strychnine were dissolved in 50 ml of 70% ethanol solution. The experiment lasted 54 minutes. There was no great change in the course of the curve.

The front of the brucine curve became less steep as the quantity of brucine decreased. The height of the column was the same (40 mm).

Having measured the potentials when synthetic mixtures were applied we were of the opinion that extracts of natural Nux vomica could be investigated by potentiometric chromatography on charcoal with advantage.
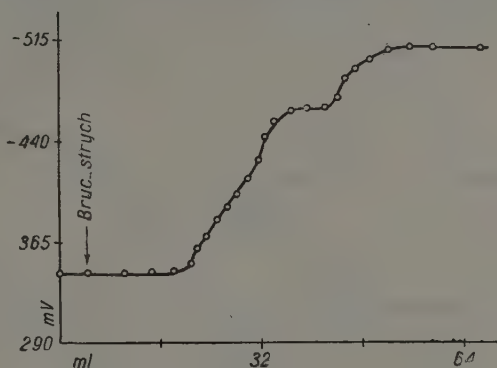

Fig. 3

An extract of poison nuts was prepared (D. A. B. VI. 234, 1938). It contained 12·9 mg of dry substances in 1 ml of solution. Fig. 4 shows the results when 3 ml of the extract, containing 38·7 mg of dry substance, were poured
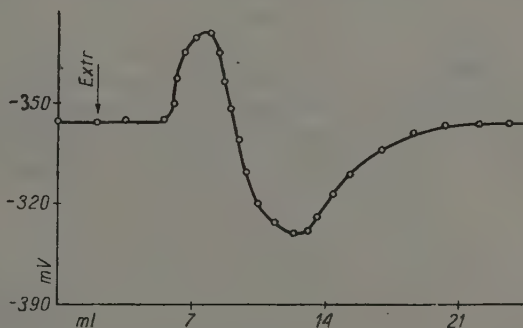
Fig. 4

onto the top of the column (50 mm high) and a 70% solution of ethanol was used as an eluent. Only two changes in the potential are visible on the diagram. The first represents the sum of the basic substances, the second that of the acid substances. The experiment lasted 39 minutes. When a degreased extract was applied (D. A. B. VI. 234, 1938) and the height of the column was doubled, a somewhat better separation of the basic and

acid substances was observed, as may be seen in Fig. 5. In this instance
3 ml of the degreased extract, containing 43·2 mg of dry substances, were
applied and 70% ethanol was used as an eluent. The experiment lasted
58 minutes. All the bases passed down the column together and only one
maximum appeared. The same may be said of the acids and their poten-
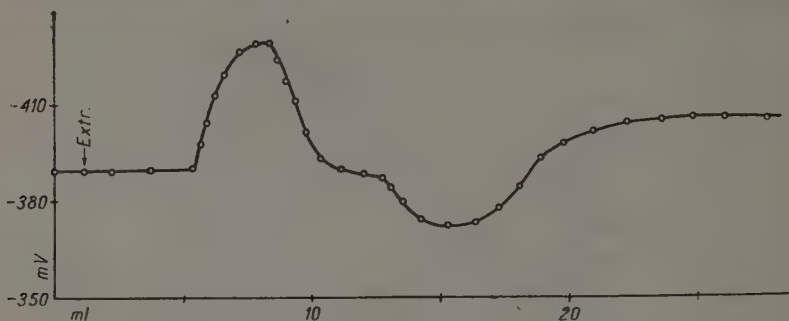
Fig. 5

tial minimum (Fig. 5). We tried the dilution method to get a better separa-
tion, hoping that the great accuracy of the potentiometric method would
give an indication of the dilute solutions of the different substances pre-
sent in the natural mixture. When the extract was diluted × 100, it gave
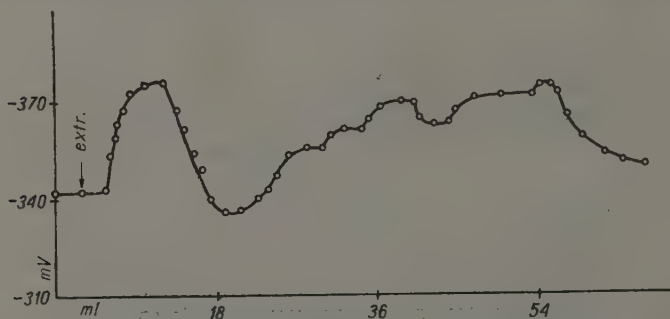
Fig. 6

much better results, as may be seen in Fig. 6. 3 ml of the diluted extract
(containing 0·43 mg of dry substances) were put on the top of a column
100 mm high. A 70% ethanol solution was used as an eluent. The first
maximum contained brucine and strychnine together. No separation of these
alkaloids is visible on the diagram (6). However, a second rise in the curve
appeared when brucine and strychnine passed down the column. This part

of the curve contains 5 steps or maxima, corresponding respectively to 5 other alkaloids. This fact recalls the similar number of steps or maxima shown in Fig. 4 of the previous paper. However, the steps are less marked here, and brucine appeared together with strychnine in one maximum. The experiment lasted 98 minutes. A comparison of the results shown in Figs. 4 and 5 of the previous paper with those shown in Fig. 6 of this paper makes it clear that aluminium oxide is more suitable for the separation of the alkaloids of the Poison Nut.
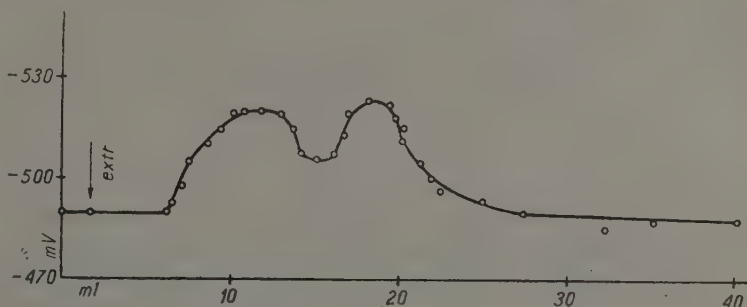

Fig. 7

On account of this fact, it was decided to carry out a new experiment. The fraction which contained brucine and strychnine in the 6th experiment was analysed on a column of purified aluminium oxide 100 mm high. The elute was evaporated to 1 ml, diluted to 3 ml with 94% ethanol, put on top of the aluminium oxide column, and then eluted with 70% ethanol. Fig. 7 shows the results. Two maxima appear on the curve. The first corresponds to brucine, the second to strychnine. The first adsorption band is lower but broader and recalls the fact that brucine is the main component of the alkaloids in the Poison Nut.

Laboratory of Physical Chemistry and Electrochemistry of the Jagiellonian University, Cracow

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Yangonin and Pseudoyangonin:
Two Isomeric Ethers of Yangonalactone

by

I. CHMIELEWSKA and J. CIEŚLAK

The work of the School of Organic Chemistry of Warsaw University on the structure of 2,4-pyronones was started by W. Lampe, who attempted to synthesize yangonin, methysticin and kavain-pigments derived from the root of Macropiper methysticum (*Radix Kawa-kawa*) [1, 2, 3].

The β-ketolactone grouping of 2,4-pyronones is capable of undergoing enolization; on account of possible tautomerism of the system, two isomeric enolic forms must be expected, as well as two types of their derivatives belonging either to the group of γ-pyrones (I) or to the group of the double unsaturated δ-lactones (II).

The ability to form stable oxonium salts with $FeCl_3$, $AuCl_3$ and H_2PtCl_6 caused W. Borsche to classify yangonin in the group of natural derivatives of γ-pyrones (flavones, flavonoles) found extensively in the plant kingdom. On the basis of degradation products, he considered that yangonin was an anhydride of the ester of 6-(p. methoxycinnamoyl)-acetylacetic acid i. e. 6-(p. methoxystyryl)-2-methoxy-γ-pyrone [13]. Borsche attributed the same structure to the synthetic compound, identical with natural yangonin [14] that he obtained in 1929.

However, Borsche's formula, proposed for this synthetic compound, seemed doubtful.

In 1939 Z. Macierewicz, working with the 6-styryl-2,4-pyronone (III), proved that the methylation product does not possess a γ-pyronone structure, but is identical with the α-pyrone compound (IV), obtained by synthetical procedure, the course of which was undoubtedly one-directional [4].

This statement was in agreement with F. Arndt [15], who considered the enolization to carbon 2 of 2,4-pyronones as impossible. However, the

properties of the natural compounds allow us to presume that this possibility exists, and so studies on the tautomerism of 2,4-pyronones have been continued by W. Lampe's co-workers [5—9].

(III)   〈   〉—CH=CH—⟨O⟩=O   (IV)   〈   〉—CH=CH—⟨O⟩=O
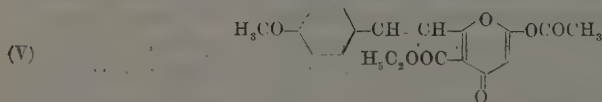   ‖   ‖
                              O   OCH₃
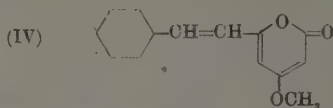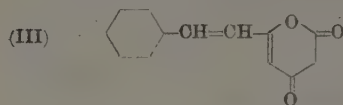
In 1951 F. Arndt, contrary to his previous statement, proved the tautomerism of benzotetronic acid and also isolated besides 4-methoxy-coumarin another isomeric ether of this acid i. e. 2-methoxy-chromone [16]. Shortly after, J. Cieślak developed a method of separating isomeric methoxy γ and α pyrones [10]. The method consisted in the precipitation from a mixture of hydrochloride of the γ form, insoluble in anhydrous ether. I. Chmielewska and J. Cieślak isolated two isomeric ethers of the 6-methyl-2,4-pyrone: 6-methyl-2-methoxy-γ-pyrone and 6-methyl-4-methoxy-α-pyrone [11]. The simultaneous investigations of S. Janiszewska-Draba-rek [12] showed that α-pyrones as well as γ-pyrones form with chloroplat-inic acid a number of stable complex salts of the same composition, but having different melting points. All the above-mentioned results rendered necessary a revision of Borsche's structural formula of yangonin.

Borsche's synthesis of yangonalactone was repeated. As a starting product we used the ethyl ester of carboethoxy yangonaic acid, obtained through the condensation reaction of p-methoxycinnamoylchloride and the sodium salt of diethyl ester of acetonedicarboxylic acid. The cyclization of the starting product in acetic anhydride gave only one acetyl derivative of 3-carboethoxyyangonalactone m. p. 104°—105°. This compound, which according to Borsche possesses the structure of 2-acetyl-5-carboethoxy-6(p-methoxystyryl)-γ-pyrone (V), does not show the basic properties character-istic for the γ-pyrone system i. e. it does not form a hydrochloride, insoluble in anhydrous ether. This property and the acidic medium in which the

(V)   H₃CO—〈   〉—CH=CH—⟨O⟩—OCOCH₃
                              |
                         H₅C₂OOC—⟨   ⟩
                                      ‖
                                      O

acid compound was prepared, show that it does not posses the structure proposed by Borsche, but must be considered as 4-acetyl-5-carboethoxy-6(p-methoxystyryl)-α-pyrone (VI).

Further steps in the synthesis of yangonalactone followed the same method as in the work cited above [14].

Methylation of the lactone by means of diazometane and separation of its isomeric ethers was achieved by the method previously described [10, 11]. An excess of diazomethane in ether was added to the suspension of 0·7 g of yangonalactone m. p. 237°—239°. An amount of 0·1 g. of the un-

reacted product (m. p. 218⁰—225⁰) was filtered off after 12 hours, and the filtrate was saturated with dry hydrochloride. Light yellow hydrochloride of the γ isomer (0·15 g.) was decomposed in the ether suspension by the

(VI)
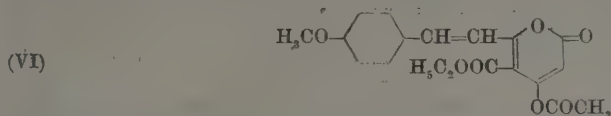
excess of diethylamine. After the evaporation of ether, 0·1 g. of 6-(*p*-methoxystyryl)-2-methoxy-γ-pyrone (VII) was obtained. The compound crystallizes from petroleum ether in the form of light yellow needles m. p. 138⁰—140⁰.

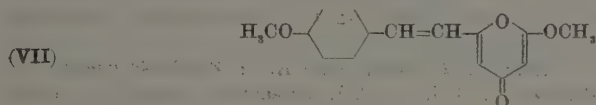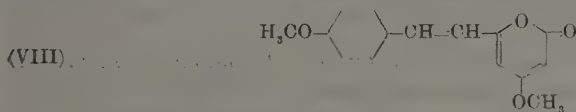The amount of the methoxy groups determined by Zeissel's method is 23·9%; calculated, it amounts to 24·03%.

(VII)

From the acidic ether filtrate, after separation of the hydrochloride of compound (VII) 0·5 g of the α isomer i. e. 6-(*p*-methoxystyryl)-4-methoxy-α-pyrone (VIII) was isolated. The above compound crystallizes

(VIII)

from diluted acetone in the form of yellow-green needles m. p. 153⁰—154⁰. The amount of methoxy groups obtained by Zeissel's method is 23·75%; calculated, it comes to 24·03%. The m. p. of compound (VIII) is in agreement with the melting point of natural yangonin given by the other authors [13].

The m. p. of the mixture of compounds (VII) and (VIII) is 130⁰—133⁰. Compound (VII) as well as compound (VIII) form complex salts with $FeCl_3$, $AuCl_3$, and H_2PtCl_6. The chloroplatinate of compound (VIII) melts at 167⁰—168⁰, i. e. at the same temperature as the chloroplatinate of natural yangonin (m. p. 168⁰—169⁰). The chloroplatinate of compound (VII) melts at 151⁰—153⁰.

The results presented above show that natural yangonin possesses structure (VIII), i. e. belongs to the group of α-pyrones. The commonly accepted γ-pyrone formula (VII) proposed by Borsche, does not represent the natural compound, but the new isomeric ether of yangonalactone-pseudoyangonin, synthesized by us for the first time.

Department of Organic Chemistry, University of Warsaw

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The Control of the Chemical Composition
of Certain Industrial Products by the Method
# of Powder-Planimetric Analysis

by

J. TOKARSKI

Communicated at the meeting of November 17, 1952

In 1939, the author devised a new method which he called the »powder-planimetric method« [1], [2] for the quantitative determination of the mineral composition of rocks. This method was first used for determining the mineral and chemical composition of rocks of magmatic origin, and was construed on the basis of the following procedure:

The rock to be analysed is pulverised. For this purpose, samples are broken off from different parts of a larger block so as to ensure their having the average mineral composition of the whole specimen. The powder obtained is sifted through a number of sieves having, for example, 900, 4900 and 10000 meshes per square cm. We can apply the planimetric method to every fraction except the finest. To do this we do not have to m e a s u r e the loose, enclosed grains of various minerals, but only to c o u n t them while shifting the samples across our microscopic field.

Practice has proved that the counting of 300 grains of one preparation is sufficient for a statistical and also chemical determination of any powder-preparation. The counting of 300 grains of every three preparations is quite sufficient for determining the mineral, and hence also the chemical composition of the rock specimen under examination. The only condition is, naturally, to know the chemical composition of minerals contained in the powder. The efficiency of this method has been confirmed by numerous tests in which, among others, a chemical analysis of the examined rock was used as a check. The details of the method which is here presented, are contained in the works cited below [3], [4].

Powder-planimetric analysis can attain a degree of precision as high as that of chemical analyses and takes a very short time to carry out. The planimetrition of one preparation does not require more than 45 minutes

and the whole analysis of a rock does not take more than three hours (three preparations).

This method has also been applied to some sedimentary rocks, among others to multi-mineral deposits of potassium salts. It has proved very useful, particularly in this last case and has given better results than ordinary chemical analysis. This is clear since, after obtaining the results of chemical analysis of solutions of potassium salts, the stechiometric binding of cations with anions may most often be brought about at will. Hence by the application of planimetric analysis we obtain the mineral composition, besides the chemical one, of a deposit. This fact becomes important in technological operations.

Below, we present another characteristic example of the possibility of utilizing powder-planimetric analysis in inorganic industry, thus achieving a great saving of time and materials.

It is well known that certain kinds of cement are composed of foundry slag and clinker. In forming the proper mixtures, one must pay great care to the mutual relationship of these two components as their function is the quality of the final product. The chemical analysis used for the control of these mixtures requires a quantitative determination of at least eight components and must be done in the shortest possible time during the rush of a factory in full operation.

It is evident that in the case of large-scale production, this control, which involves great responsibility on the part of the controller, requires the instalation of a special laboratory to cope with the large amount of work involved.

The author, having at his disposal slag, clinker and a mixture of so-called foundry cement, proves that in place of chemical analysis, one may here apply, with excellent result, the method of powder-planimetric analysis. The proofs of this are set out below.

In the enclosed table we have listed in columns 1, 2 and 3 the chemical analyses of slag, clinker and cement mixture (foundry cement) as made

TABLE

of chemical analyses of slag, clinker and foundry cement

$^{0}/_{0}$	Slag		Clinker		Foundry cement		Powder anal.	
	1	1a	2	2a	3	3a	pl. 1	pl. 2
SiO_2	37·30	37·70	23·64	23·59	25·4	25·6	25·5	26·3
R_2O_3	12·80	13·45	6·52	6·43	8·2	7·2	7·4	7·9
CaO	44·11	44·50	67·67	67·50	64·4	64·1	64·2	62·9
MgO	3·84	3·88	1·34	1·77	1·8	2·2	2·1	2·2
SO_3	—	—	—	—	—	—	—	—
Others	1·84	0·50	0·64	1·71	0·2	0·8	0·8	0·7

by the factory. In columns 1a, 2a and 3a we have similar analyses, made by the Soil Science Institute of Cracow University. In column pl. 1 we have the chemical analysis of foundry cement, obtained by the powder-planimetric method; in column pl. 2 the same chemical analysis for 20% cement.
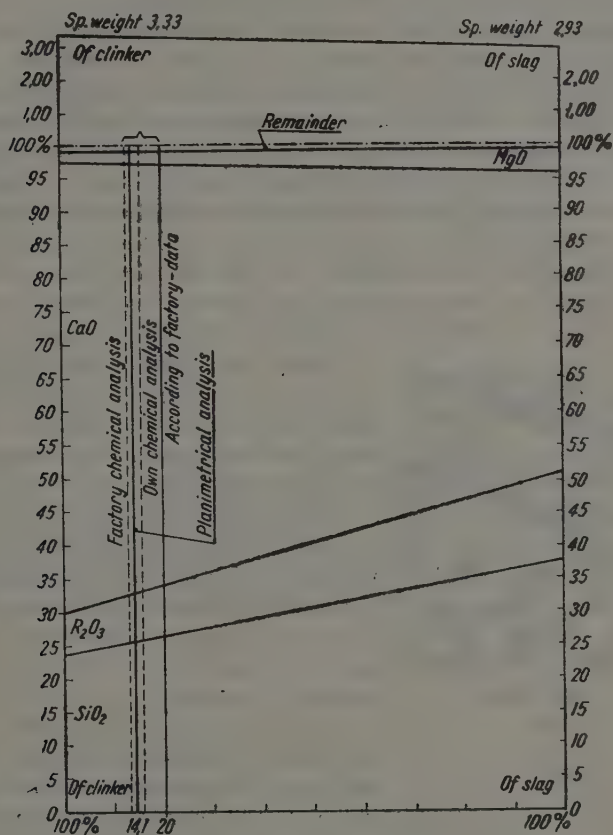
Fig. 1

The cement which was sent to be analysed was said to contain 20% slag. The chemical composition of each mixture composed of various quantities of slag and clinker of known chemical composition can be theoretically deduced from the enclosed example of a »control diagram«, in which the ordinates show the weight percentages of the components of the slag and clinker, according to the data set forth in the table of chemical analyses. By connecting these percentile segments by straight lines, we were able to show on the diagram the fields of variability of the che-

mical composition of each mixture. Two of the chemical analyses of cement, were plotted in the diagram: our own analysis and that which came from the factory; they are represented by dotted lines. Besides this, we drew two straight lines, whose place in the diagram was determined by plani-metric analysis. One of them corresponds to a planimetric analysis which showed the presence of $14 \cdot 1^0/_0$ of slag in the cement, the other to a plani-metric analysis of cement said to contain $20^0/_0$ of slag (continuous lines).

As may be seen from the drawing, the results of planimetric analysis of cement lie between the two chemical analyses, i. e. the chemical com-position of cement, arrived at by this analysis, corresponds to the average of two closely comparable analyses. Planimetrical control of the slag that was sent in, proved that it did not contain $20^0/_0$ of slag as was claimed. Had that been the case, its chemical analysis would have shown a chemical composition similar to that shown in column »pl. 2« of the above table.

In microscopical preparations of the materials that were received, one could very easily and simply discern the difference between the grains of slag and clinker. The first were colourless, perfectly transparent, irregular in shape and closely resembled particles of glass with a high coefficient of light re-fraction. The grains of clinker, though si-milar in shape, were, nevertheless, opaque and black (see illustration).

Of slag   **Of clinker**
15% mixture

Fig. 2

The special investigations of synthetic mixtures, composed of various weighed quantities of slag and clinker (containing 1 to 20 per cent. of slag) showed that;

1) a planimetric analysis of mixtures, made by counting off 900 grains, took 15 minutes to perform;

2) the accuracy of planimetric deter-mination in relation to weighed quantities of components lay within the limits of $0 \cdot 2^0/_0$;

3) the accuracy in the calculations of the chemical composition of mix-tures from the »control diagram«, when compared with the accuracy of the actual chemical analysis, remained within the limits of admissible error for the latter.

Moreover, powder-planimetric analysis in its application to the control of cement production, is irreplaceable as regards one important point.

Devitrified slag loses its hydraulic qualities and can be controlled in this respect only with the aid of a polarizing microscope. One may then distinguish the degree of partial or complete devitrification on the basis of a differentiation of crystallites, reacting to polarized light. The chemical analyses of crystalline and amorphous slag do not show any such diffe-rences.
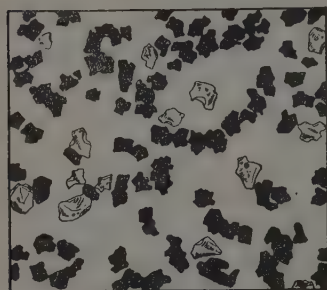
Finally, we must note that in the case described above of the control of foundry cement, powder-planimetric analysis revealed the faults, both in the analysis of one of the components, and in the proportional composition of the mixture.

It is clear that the powder-planimetric method does not exclude the need for chemical investigations. The basis for constructing a control diagram is the chemical analysis of slag and clinker which are used as the essential coordinates. By the method described here one can control only the manufacture of mixtures by hand or by machine and the degree of devitrification of slag. However, there is no doubt that the elementary chemical analysis of the components of cement (slag and clinker) could be replaced by a microscopical analysis, based, for instance, on the fixing of the coefficients of light refraction of various slags and clinkers. Such a method is already being applied with good efects in petrographic work. However, we do not propose to deal with this problem in the present paper.

Institute of Soil Science, Jagiellonian University, Cracow.

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The Genesis and Systematic Position of Bentonites

by

J. TOKARSKI

Communicated at the meeting of February 23, 1953

Within the sedimentary crust of our planet about 82% of clay minerals have been found.

Interest in these minerals grew during the 20-th century, particularly when it became known that they play an important role in many fields of practical knowledge, as, for example, in the ceramic industry, in soil science, in land surveying, and so on.

The development of microscope technique, the use of the electronic microscope and powerful, penetrating X-rays, have greatly aided in the investigation of clay materials, and, in many cases, have led to sufficient knowledge of their structure and, consequently, to an explanation of some of their special physico-chemical properties.

Of the principal clay minerals appearing in sedimentary rocks, two groups, viz. the m o n t m o r i l l o n i t e and the k a o l i n i t e, form the highest percentage. In the last 30 years it was possible to establish the following facts concerning especially the first one:

1. the montmorillonite group forms a series of isomorphically bound links, with montmorillonite, beidellite, nontronite, hectorite and saponite as chief members,

2. the afore-mentioned minerals possess a uniform chemical structure. They permanently bind 10 oxygen anions and 2 hydroxyl groups, disposing of 22 negative charges with such a quantity of silicon, aluminium, ferric and ferrous iron, magnesium and other cations as makes the sum of their positive charges equal, or very nearly equal, to 22. The differentiation in chemical composition of the isomorphs of the group in question is brought about by maintenance of the above-mentioned principle of valency-equilibrium, by the varying proportion of different cations.

3. in the crystal lattice of the mineral series already referred to, there appear 2 co-ordinative groups, viz., the tetrahedral, which is formed by silicon and part of aluminium cations, co-ordinated with 4 oxygens, and

the octahedral, formed by the remaining cations co-ordinated spatially with 6 oxygen and hydroxyl anions.

The whole crystal lattice is here of the layer type and has the structure of pyrophyllite, with the chemical composition:

$$Al_2O_3 \cdot 4SiO_2 \cdot H_2O \text{ or that of talc: } 3MgO \cdot 4SiO_2 \cdot H_2O.$$
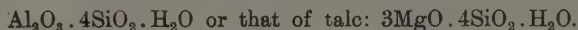
4. the partial replacement of the silica cation by aluminium in the tetrahedral coordinations causes an excess of negative charge inside the lattice. This excess is balanced by exchangeable cations, chiefly Na and Ca, which appear on the surface of the structural layers.

5. in the detailed study on the montmorillonite group, based on investigation of 100 selected samples of minerals belonging to them, we found in a work by C. S. Ross and S. B. Hendricks [1] the original formulae which considerably facilitate comparison of the analytical data concerning clay minerals. The following abbreviated formula was here adopted:

$$\left[Al_{a-y}^{+3} + Fe_b^{+3} + Mg_d^{+2}\right]\left[Al_y^{+3} + Si_{4-y}^{+4}\right]O_{10}\left[OH\right]_2 x \cdot 33$$
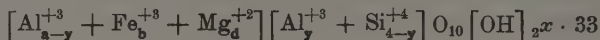
where $a-y, b, d$, and Si_{4-y} denote the proportions within the cations given in the formula.

6. the so called »bentonite«, frequently occurs in the montmorillonite group. Essentialy it is a magnesium-aluminium montmorillonite, whose genesis is closely connected with the hydrolitic decomposition of volcanic glass of basic or slightly acid rocks (rhyolite, rhyodacites, etc.). It is obvious that in places where such vitreous fragments collected during volcanic eruptions in the form of pure tuffs, the formation of montmorillonite took place in an exceptionally »pure« medium. Hence there also arose montmorillonite elements free of fortuitous impurities, which presented for analysis ideal examples of their chemical and physical structure.

7. the important results of all investigations of the montmorillonite group showed that there exists a strict dependence between the nature of clay minerals and conditions giving rise to their formation. Until now, all the evidence seems to prove that, generally speaking, rocks containing alkaline feldspars and micas, when subjected to hydrolysis, yield kaolinite derivatives, while basic rocks, rich in dark components, calci-feldspars, and volcanic glass, yield derivatives of the montmorillonite group. Departures from this rule may occur, depending on climatic conditions and on the length of time the hydrolysis lasts. An important parallel medium in which the forming of the montmorillonite group was confirmed is a soil possessing a special hydrolitic factor in the form of humus acids.

Bentonites are also known in Poland. They have been discovered, among others, in the Tortonian layers near the Vistula. Here they form very small deposits among other formations, but samples were taken from places where they were concentrated in somewhat greater quantities. We re-

cognised their presence, too, in layers of the same period in the Ukrainian Socialist Soviet Republic in the neighbourhood of Lwów, Krzemieniec and other places, and the first analyses [2], [3] were made of samples taken from those places.

Independently of these, other analyses were made of tuffs and tuffites which appear in numerous places in the Carpathian foothills. Recently an analysis was made of bentonite from the district of Chmielnik.

These analyses provided sufficient data on which to base the following explanation of the genesis and systematic position of the minerals previously referred to:
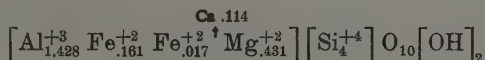
1. energetic volcanic activity, which during the Tortonian period strongly affected the inner arc of the Carpathians, caused a considerable area of the ramparts of this mountain range to be covered by pyroclassic tuff material, composed mainly of pure volcanic glass of rhyodacitic and rhyolitic origin. This material, blown by south winds, became mechanically segregated, with the result that in the areas near the Carpathians it became composed of coarser grains, whereas in the north it formed concentrations of fine silt. Probably the original tuffs were already partly hydrolysed before being scattered northwards.

The analytical data concerning sub-Carpathian volcanic glass preserved in its primordial state, confirmed their close correlation within the already known montmorillonite groups.
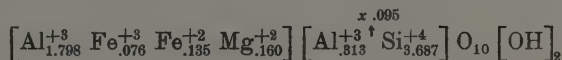
An incontestable proof of this correlation was provided by the microscopic analysis of identical phenocrysts, such as zircon, pyroclastic quartz, feldspars, and above all, basaltic hornblende, which were present in all the materials. In bentonites, distinct traces of volcanic glass were found in the residues insoluble in HCl, which was also a proof of their linkage with tuffs.

2. the chemical analysis of bentonite from Chmielnik and from near Lwów is presented below in a new chemical structural form.

Bentonite from Chmielnik:

$$\left[Al^{+3}_{1.428}\ Fe^{+2}_{.161}\ Fe^{+2}_{.017}\ \overset{Ca\ .114}{Mg^{+2}_{.431}}\right]\left[Si^{+4}_4\right]O_{10}\left[OH\right]_2$$

Bentonite from near Lwów:

$$\left[Al^{+3}_{1.798}\ Fe^{+3}_{.076}\ Fe^{+2}_{.135}\ Mg^{+2}_{.160}\right]\left[\overset{x\ .095}{Al^{+3}_{.813}}\ Si^{+4}_{3.687}\right]O_{10}\left[OH\right]_2$$

A comparison of these formulae shows that the material from Chmielnik corresponds to the montmorillonite link, whereas that from near Lwów corresponds to beidellite. The bond between the above-mentioned bentonites and sub-Carpathian volcanic tuffs is clearly shown, too, by comparing the above formulae with an analogous formula based on the results of chemical analysis of a colloid separated from tuffs which were obtained from a boring in the Carpathian foothills.

The formula for the colloid approximates very closely to that for Chmielnik bentonite and serves also as a formula for montmorillonite.

Colloid from sub-Carpathian tuff:

$$\left[Al^{+3}_{1.380} \; Fe^{+3}_{.091} \; Fe^{+2\;\overset{x\,.084}{\uparrow}}_{.199} Mg^{+2}_{.248} \right] \left[Si^{+4}_4 \right] O_{10} \left[OH \right]_2$$
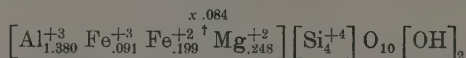
3. According to all geochemical data, it would appear that the presence of magnesium in the parent rocks favours the coming into being of the links of the montmorillonite group. Their genesis would, therefore, seem to be connected with the hydrolysis of rocks rich in femic or so-called basic components.

The American view, viz., that in the case of an insufficient quantity of magnesium in rocks undergoing transformation into montmorillonite, this element could be supplied from an outside source, e. g. from sea-water or from magnesium carbonates present in the soil profiles, is false.

During hydrolysis of any kind of volcanic glass containing even minute quantities of magnesium there is always the possibility, depending of course upon environmental conditions, of the formation of montmorillonite in a corresponding quantity.
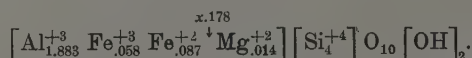
The excess of silica freed during the hydrolysis of volcanic glass may either be removed during the process of diagenesis or may remain as a residual »impurity« of the montmorillonite which has been produced.

We offer the following proof in support of our argument.

During our experiments with sub-Carpathian tuffs, we also made an analysis of pure volcanic glass which had been isolated from tuffite sediments. This glass contained: 78.72% SiO_2, 12.09% Al_2O_3, 0.64% Fe_2O_3, 0.92% FeO, 0.10% MgO, 1.07% CaO, 1.88% K_2O and 3.48% Na_2O. On account of the high excess of silica, it was not possible, of course, to present the analysis of this material, directly, in terms of the formula of any montmorillonite link.

It was possible only when the quantity of silica was reduced to the amount sufficient for the linkage of silica, without the addition of aluminium, with oxygen in tetrahedral coordination.

A corresponding formula, similarly deduced from the above-mentioned glass, for the montmorillonite »potentially« contained in it, would be:

$$\left[Al^{+3}_{1.883} \; Fe^{+3}_{.058} \; Fe^{+2\;\overset{x.178}{\downarrow}}_{.087} Mg^{+2}_{.014} \right] \left[Si^{+4}_4 \right] O_{10} \left[OH \right]_2.$$

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Preliminary Revision of the Stratigraphy
of the Pieniny Klippen-Belt Series in Poland

by

K. BIRKENMAJER

Communicated by M. KSIĄŻKIEWICZ at the meeting of March 16, 1953

According to the generally accepted view, the sediments of the Pieniny Klippen-belt can be divided into two distinct series: the Klippen series and the mantle series. The Klippen series is further subdivided into the several Klippen series proper and some associated series; to the first group (Pienids) belong: the Czorsztyn series, the Pieniny passage series (with several facial types, such as: the Kýsuca, the Podbiel, and the Pruské facial type) and the typical Pieniny series. With these proper Pienids are associated various sedimentary series of non-Pieniny derivation, such as the High-Tatra series (Manin-Haligovce series) and the Sub-Tatra series (Kostelec series), which are incorporated into the present structural composition of the Pieniny Klippen-belt. According to this same view, the Czorsztyn series represents the sediments from the Aalenian to the Tithonian; younger members than the Tithonian are absent, owing to the post-Tithonian emersion. The Pieniny series consists of stratigraphic members ranging from the Trias resp. from the Lias, or the Lower Dogger to the Lower Aptian. The uppermost Neocomian is unknown in all the Klippen series. The Klippen series are covered directly by the second Albian horizon (Leymeriellan), or by higher members of the Middle Cretaceous, belonging to the mantle series [1].

During the lacune Upper Aptian-Lowest Albian the Pienids were folded ("Pieniny phase" of D. Andrusov) into two structural units of nappe character: the lower unit, named the Czorsztyn nappe, thrust over from the south by the upper unit called the Pieniny nappe with digitations: the lower — passage Pieniny nappe and the upper — typical Pieniny nappe. The Pieniny nappe was thrust over by the Manin unit, which belongs to the High-Tatrid elements. The folded structure was transgressively covered by the older mantle sequence composed of the Albian and Cenomanian. According to D. Andrusov and L. Horwitz this sequence does not show any segregation

into series which could be correlated with the Klippen series. Because the Albian sediments are of pelagic character, and no signs of abrasion or erosion older than the Albian can be detected in the beds, D. Andrusov supposed that the Pieniny stage had been of short duration, had occured below sea level and had brought no emersion. So far, no section has been discovered in which the unconformity between the older mantle series and the underlying Pienids is visible.

According to the writers already cited, the first emersion of the Klippen zone took place during the Turonian — Lower Santonian. In the Upper Santonian the transgression depositing the younger mantle series commenced (Senonian-Early Tertiary).

The writer, during his field work, found beds representing the Neocomian of the Czorsztyn series; thus the lacune presumed by preceding, writers does not exist. On the contrary, both in the Czorsztyn series and in the Pieniny series (both in the type and passage series) slow transition and conformity between the Klippen sequence (Tithonian and Neocomian) and the Middle Cretaceous have been noted. These observations refute the existence of the "older mantle series" (Albian — Cenomanian) and the Pieniny orogenic phase. The Albian and the Cenomanian belong to the Klippen series; thus the period of first folding movement has been shifted to the post-Cenomanian time, synchronous with the folding in the Tatra Mts. At the same time the possibility of the existence of the Albian, which, according to L. Horwitz, does not occur in the Polish part of the Pieniny Klippen, should be emphasized [2].

The Klippen series are divided, on the basis of ca. 40 profiles, into four tectonic and facial units. The division concerns the Pienids sequence. The highest of these units is the Pieniny series, the lowest — the Czorsztyn series, the intermediate are named the Branisko and Niedzica series (passage series). In the sedimentary basin of the Pieniny belt, the Pieniny series probably occupied the southernmost position; to the north were situated the Branisko and Niedzica series and the Czorsztyn series in the most northern part. During the post-Cenomanian movements these series were thrust over each other as separate nappes and subsequently covered by the Senonian transgression.

The age determination of particular lithologic members of the Klippen series is in many instances based only on convention because of the scarce, poorly preserved and only partly determined fauna. With regard to the Upper Jurassic, Neocomian and Middle Cretaceous, micropalaeontological methods have been adopted with fairly good results. On the whole it is very difficult to establish a complete stratigraphical profile because of the tectonic complexity of the Klippen-belt. Sections with a complete stratigraphic sequence are practically unknown. Fragmentary sections may be compared with one another with the help of a general tectonic concept if there exists any similarity in the sequence of lithologic members. Of course, there is

a strong hypothetical element in the results achieved and many existing doubts can only be eliminated after prolonged field research.

The Pieniny series corresponds exactly to the typical Pieniny series of D. Andrusov. Within the limits of the Polish Pieniny Klippen-belt it occurs in the Dunajec valley (Peak of Trzy Korony) and around Maruszyna-Szaflary on the lines of transversal depressions. It consists of stratigraphic members between the Domerian and the Cenomanian. The most characteristic components of this series are: The Posidonomya shales (Aalenian) strongly developed, the supra-Posidonomya beds (Bajocian-Bathonian), the "manganese" and green radiolarites (Callovian-Kimmeridgian) and light, cherty limestones (Hornsteinkalk of V. Uhlig), which contain Calpionella in their lower part (Tithonian-Berriasian), while the upper portion abounds in Radiolaria. The last-named member forms the most characteristic element of the Pieniny series. The uppermost members of the Neocomian and Middle Cretaceous are similarly developed as in other Klippen series. Within the area of the Polish Pieniny Klippen-belt, this series exhibits a very constant stratigraphic development.

The Branisko series is probably equivalent to the Kýsuca series of D. Andrusov. It derives its name from the highest peak on the Polish Spisz (Branisko 879 m). Of all the Klippen series this one plays the most important part in the formation of the Polish Pieniny. It occurs around Szczawnica, extending from Sromowce Wyżne and Szaflary (Polish Spisz) to Stare Bystre. Besides the members common with the Pieniny series, it contains some horizons approaching the Niedzica and Czorsztyn series. In the lower portion of the Aalenian there occur beds in Flysch facies, while the upper part of that stage is represented by shales with concretionary siderites (locally?); the green radiolarites are covered by red ones and by concretionary, red or variegated limestones of small thickness. The uppermost Neocomian and the Middle Cretaceous are similar to the other series. Like the Pieniny series, the Branisko series possesses a fairly uniform stratigraphical development; in some parts it strongly approaches the Niedzica series.

The Niedzica series is named after the village and castle of Niedzica. It occurs in the area Czorsztyn-Niedzica-Falsztyn, north of Trzy Korony Peak and around Jaworki. Because of strong tectonic reduction it is very difficult to establish its stratigraphy. The Niedzica series is closely related to the Czorsztyn series, from which it differs however, by reason of the presence of the index horizon of variegated radiolarites; it contains less differentiated Tithonian and feebly-developed cherty limestones in the Neocomian. The following members are common with the Czorsztyn series: the opalinus marls and murchisonae shales of the Aalenian, the white and red crinoidal limestones of the Dogger, the nodular limestones (Knollenkalk of V. Uhlig) of the Upper Jurassic, the Upper Neocomian and the Middle Cretaceous. The clays with exotic blocks which occur at Czorsztyn (considered by L. Horwitz, 1938, to be the Santonian), must be included in the Niedzica

series, because they contain *Exogyra columba* LAMK and are connected with the Globotruncana marls of the Cenomanian. The presence of two horizons of nodular red limestones separated by radiolarites constitutes perhaps the most characteristic feature of the Niedzica series. The Klippen of Podbiel — (Červený Kameň), the Pruské (Podhradský stream) series and the Klippen of Oravský Castle in Slovakia, described in D. Andrusov's papers may be regarded as being equivalent to the Niedzica series.

The Czorsztyn series corresponds to the "série subpiénine ou de Czorsztyn" of D. Andrusov. The profile of the Klippe of Czorsztyn Castle described by V. Uhlig (1890) and completed by the author may be regarded as typical for this series. The Czorsztyn series extends from Rogoźnik, through Szaflary, Nowa Biała, Krempachy and Falsztyn, to Czorsztyn, and, after a long break, occurs again around Jaworki and Biała Woda. Only the upper members of the Neocomian and the Middle Cretaceous of the Czorsztyn series are common with the Pieniny series, and with the Branisko one — besides these are: the shales with siderites of the Aalenian, the facies of the red, nodular limestone in the middle portion of the Upper Jurassic and the Flysch horizon of the Aalenian. A great resemblance exists between the Czorsztyn and Niedzica series. The most characteristic feature of the Czorsztyn sequence and one that is unknown in other series is the presence of brachiopodal limestones, shelly limestones with ammonites and detrital and crinoidal limestones occuring in the Tithonian.

No radiolarites occur in the Czorsztyn series lying within the Polish part of the Klippen-belt. The lower Neocomian of the series is represented by marls and marly limestones with Globigerina and Radiolaria and with cherts which correspond to the cherty limestones of other Klippen series The Upper Neocomian and the Middle Cretaceous are developed like corresponding members in other series. In the Czorsztyn series a Flysch horizon occurs in the Lower Aalenian, just as in the Slovakian part of the Klippen-belt. This horizon was regarded by L. Horwitz as belonging exclusively to the Pieniny passage series.

Institute of Physical Geology, Academy of Mines and Metallurgy, Cracow

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Preliminary Revision of the Stratigraphy of the Pieniny-Klippen-Belt Series in Poland
(K. Birkenmajer 1953)

Stage	PIENINY SERIES — Sokolica, Trzy Korony, Żłobiny, Sromowce Wyż., Niż., Maruszyna (Ranysborg)	BRANISKO SERIES — Falsztyn (Branisko), Niedzica (Kapuśnica), Czorsztyn (Harcygrund, Flaki), Jarmuta	NIEDZICA SERIES — Village Niedzica	NIEDZICA SERIES — Kosarzyska Valley near Falsztyn	NIEDZICA SERIES — Niedzica Castle	NIEDZICA SERIES — Upper Homole Gorge	CZORSZTYN SERIES — Czorsztyn, Falsztyn, Jaworki, Biała Woda, Krempachy, Szaflary, Rogoźnik
CENOMANIAN	12. Cenomanian Flysch: fine-grained, hieroglyphic sandstones of bluish or green-yellow colour, interbedded with sandy marls of like colour. 11. Globotruncana Marls: in the lower part cherry-red and green marls with finely divided muscovite. *Rotalipora apenninica*; in the upper part cherry-red marls interbedded with greenish sandstones.	13. Cenomanian Flysch: fine-grained, hieroglyphic sandstones of greenish and grey colour, often with plant detritus. 12. Globotruncana Marls: green and often spotted marls with *Rotalipora apenninica*, green and variegated marls.	?	12. Cenomanian Flysch: thin-bedded, hieroglyphic sandstones of grey-green and bluish colour. 11. Globotruncana Marls: green marls, slaty, marly limestones with *Rotalipora apenninica*, cherry-red and variegated marls.	12. Cenomanian Flysch: thin-bedded, hieroglyphic sandstones and sandy, exotic-clays with *Exogyra columba* (According to L. Horwitz, 1938 — Santonian). 11. Globotruncana Marls: green and variegated (cherry-red and green) marls with *Rotalipora apenninica*.	?	14. Cenomanian Flysch: fine-grained, hieroglyphic sandstones greenish or bluish. 13. Globotruncana Marls: green, sometimes spotted marls with *Rotalipora apenninica*, and variegated (cherry-red and green) marls, sometimes grey and black.
ALBIAN / APTIAN / BARREMIAN	10. Sideritic Marls: thin-platy marls and marly shales, bluish-grey, yellow when weathered, with finely divided muscovite and rare intercalations of siderites. 9. Beds with Globigerina and Radiolaria: limestones, marly shales and marls, in lower part black, in the upper portion blacky-green, spotted and green. Fine muscovite in the upper part.	11. Beds with Globigerina and Radiolaria: marly shales and marls, green spotted, grey marly siltstones, black limestones. In the lower part abundant *Radiolaria*, in the upper one — *Globigerina*.		10. Beds with Globigerina and Radiolaria: b. shaly marls, green, spotted, with intercalations of black pyritic marly shales and limestones (fauna of retrogressive ammonites). a. marly shales, black siliceous limestones with *Radiolaria* and grey Globigerina-siltstones.	10. ?		12. Beds with Globigerina and Radiolaria: b. Without cherts: marly shales and marls black and greenish, spotted with abundant *Globigerina* and *Radiolaria*.
HAUTERIVIAN / VALANGINIAN	8. Cherty Limestone: bedded, light-grey limestone, in the lower part feebly-, in the upper part — strongly spotted. Near the top dark colour and intercalations of black, thin shales appear. The limestone contains bands of brown-bluish or black cherts.	10. Cherty Limestone: bedded, light-grey limestone, in the lower part feebly — in the upper one — strongly spotted. Near the top intercalations of black, thin shales appear. The limestone contains bands of black cherts. Abundant *Radiolaria*.		9. Cherty Limestone: bedded limestones of small thickness with *Radiolaria*, white or greenish, with bluish and black cherts.	9. ?	8. „Pseudo-cherty" Limestone: bedded, light-grey or light-green limestone at places pink, siliceous, slightly marly, with *Radiolaria*.	a. With cherts: marly limestones interbedded with marls, black and green, often spotted. In limestones bands of cherts. Abundant *Globigerina* and *Radiolaria*. 11. Beds with Globigerina: shaly or concretionary marly limestones and marls of red colour with *Globigerina* of small thickness.
BERRIASIAN	7. Cherty Limestone with Calpionella: b. light-yellow, bedded limestones with bands of brown-bluish cherts. Numerous *Tintinnidae*.	9. Cherty Limestone with Calpionella: b. light-yellow, bedded limestones with bands of bluish and black cherts. Numerous *Tintinnidae*,		8. Upper Nodular Limestone:		7. Calpionella Limestone: feebly bedded limestone, pale-pink, or yellowish or greenish, with *Tintinnidae*.	10. Crinoidal Limestone of Tithonian-Berriasian: deep-red, pink and green or greenish crinoidal limestone with no quartz. 9. Brachiopodal Limestone: light-pink or yellow limestone containing brachiopods, crinoids and *Aptychi*. Shelly beds composed of *Aptychus* frequent. Shelly limestones with ammonites of Rogoźnik presumably corresponds to this horizon.
TITHONIAN	a. light-green or grey, bedded limestones with brown-bluish cherts.	a. light-greenish or white limestone with rare bands of bluish, black, seldom red or green cherts. *Tintinnidae* very abundant.	4. Upper Nodular Limestone: b. With Calpionella: light red limestone, concretionary or bedded with *Tintinnidae*.	b. With Calpionella: red or light-red, concretionary or bedded limestone with rare ammonites and belemnites. Abundant *Tintinnidae*.	8. Calpionella Limestone: light-yellow, pink or cream-yellow limestone with *Tintinnidae*. 7b.	6. Upper Nodular Limestone: b. With Calpionella: pale-pink, red or green limestone with *Tintinnidae*.	8. Calpionella Limestone: light-yellow, sometimes with rare crinoids unbedded limestone with numerous *Tintinnidae*. 7. Nodular Limestone: b. With Calpionella: concretionary but bedded red limestone of small thickness with *Tintinnidae*.
LOWER MALM (CALLOVIAN-KIMMERIDGIAN)	6. Green Radiolarites: green or bluish-green, usually calcareous cherts and green siliceous limestones. Exceptionally (Trzy Korony Peak) also thin, red radiolarites and siliceous limestones at the top of the horizon. 5. „Manganese" Radiolarites: cherts and siliceous shales grey-green, brown, greenish, usually limeless. Abundant tarnish of manganese compound, black-bluish in colour.	8. Nodular or Pseudo-concretionary Limestone: of small thickness, bedded or concretionary limestone with lenses of cherts red and green in colour. 7. Red Radiolarites: red, usually calcareous cherts. 6. Green Radiolarites: green cherts, green siliceous limestones, green-brownish and green-red cherts. 5. „Manganese" Radiolarites: cherts and siliceous shales green-bluish, grey-greenish, spotted, slightly calcareous. Abundant tarnish of manganese compounds, black-bluish in colour.	a. Without Calpionella: red limestone concretionary or bedded with rare ammonites.	a. Without Calpionella: red concretionary or bedded limestone. In the lower part bands of red radiolarites (ammonites, belemnites). 7. Red Radiolarites: red, brown and orange yellow cherts. 6. Green Radiolarites: green, green-red, green-bluish cherts. 5.	7a. Upper Nodular Limestone (without Calpionella): light-red, concretionary limestone composed of calcareous concretions and hematite-calcareous cement (ammonites poorly preserved). 6. Red Radiolarites: red, feebly calcareous cherts and thin siliceous limestones of like colour. 5. Green Radiolarites: green, green-blue and greenish-brown cherts feebly calcareous and siliceous limestones. 4. Lower Nodular Limestone: dark-red, concretionary limestone composed of calcareous concretions with hematite-calcareous cement (belemnites). 3. Red Crinoidal Limestone: dark-red crinoidal limestone of small thickness.	a. Without Calpionella: red, concretionary limestone, strongly cemented with hematite-calcareous cement (ammonites, belemnites). 5. Variegated Radiolarites: calcareous red and green-bluish cherts. 4. Lower Nodular Limestone: dark-red, concretionary limestone composed of calcareous concretions with hematite-calcareous cement (ammonites, belemnites). 3. Red Crinoidal Limestone: red or yellow crinoidal limestone with quartz and fragments of carbonate rocks.	a. Without Calpionella (Czorsztyn limestone): deep-red, concretionary limestone. Concretions joined together with hematite-calcareous cement. Fairly abundant ammonitic fauna of horizons (V. Uhlig 1890): *Reineckia greppini, Peltoceras transversarium, Aspidoceras acanthicum*. 6. Red Crinoidal Limestone: red pink, seldom yellowish or greenish bedded or shaly limestone, usually containing abundant quartz grains. Fossils very infrequent (horizon *Oppelia fusca*).
BATHONIAN	4. Supraposidonomya Beds: light-browny or bluish limestones with black spots. (According to L. Horwitz, 1937, contain a Middle Bajocian fauna).	4. Supraposidonomya Beds: brown or grey-bluish limestones with brown-black spots, interbedded with marly shales of like colours. (According to L. Horwitz, 1937, they contain a fauna of the Middle Bajocian). Also grey and bluish, spotted sandy-muddy limestones at places silicified.	1. Lower Nodular Limestone: lime concretions cemented with hematite-calcareous cement with belemnites, brachiopodes and ammonites (*Parkinsonia sp.*)	4. Red Crinoidal Limestone: bedded, of small thickness red crinoidal limestone. 3. White Crinoidal Limestone: yellowish and white crinoidal limestone of small thickness.	3. Red Crinoidal Limestone: dark-red crinoidal limestone of small thickness. 2. White Crinoidal Limestone: white or yellowish crinoidal limestone of small thickness.	2. ?	6. Red Crinoidal Limestone (as above). 5. White Crinoidal Limestone: unbedded, white, grey, pink or yellow crinoidal limestone. Abundant grains of: quartz, bluish dolomites and limestones. Fossils infrequent (brachiopods, belemnites)
BAJOCIAN							
AALENIAN — Ludwigia murchisonae		3. Shales with Siderites: (? locally): black shales of small thickness with small sideritic concretions. At the top a bed of spotted limestones.		2. Shales with Siderites: shales, occasionally calcareous of green-black colour, with sideritic concretions.	1. Shales with Siderites: black shales shaly clays and clays with sideritic concretions.	1. Shales with Siderites: black shales with sideritic concretions.	4. Shales with Siderites (Murchisonae Shales): black marly shales, shaly clays and clays with small sideritic concretions. Fauna of *Ludwigia murchisonae* horizon.
AALENIAN — Leioceras opalinum	3. Posidonomya shales: marly, black shales with fine muscovite and uneven fracture. Abundant *Posidonomya alpina*, *Harpoceratidae*, *Belemnitidae*.	2. Posidonomya Shales: marly shales, grey, grey-black with finely divided muscovite and uneven fracture. Often *Posidonomya alpina*, rare *Harpoceratidae*. 1. Flysch Aalenian: black and grey sandy shales and thin-bedded sandstones, strongly micaceous. Sandstones are hieroglyphic and graded. Rare coal seams, often ferrous sulphides.		1. Opalinus Marls: marls, marly shales and marly limestones, bluish-grey, spotted, with finely dispersed muscovite and *Harpoceratidae*.	?		3. Opalinus Marls: grey, grey-bluish, commonly spotted marls and marly limestones with finely divided muscovite. Fauna of *Leioceras opalinum* horizon. 2. Flysch Aalenian: sandy shales interbedded with sandstones grey or black, strongly micaceous, with grey, crinoidal limestones in the lower part and coal seams in the upper one. *Posidonomya alpina*.
TOARCIAN	2. ?						1. „Subflysch" Beds: limeless, green and green-and-black shales with black-bluish tarnish of manganese compounds with sideritic and Fe-sulphides concretions.
DOMERIAN	1. Spotted limestones and grey or bluish marls with *Amaltheus margaritatus* (L. Horwitz 1937).	?					
— PLIENSBACHIAN TRIAS —	?						?